



INVESTICE DO ROZVOJE VZDĚLÁVÁNÍ

**Vysoká škola báňská – Technická univerzita Ostrava**



# **MATERIALS FOR ELECTRICAL ENGINEERING**

**Chosen chapters**

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# CONTENT

|  |           |
|--|-----------|
| <b>1. CONDUCTIVE MATERIALS</b>   | <b>4</b>  |
| 1.1 Highly conductive materials for electrical engineering                 | 4         |
| 1.1.1 Copper   | 5         |
| 1.1.2 Copper alloys  | 7         |
| 1.1.2.1 Copper-zinc alloys   | 7         |
| 1.1.2.2 Copper tin alloys  | 8         |
| 1.1.2.3 Special copper alloys  | 11        |
| 1.1.3 Aluminum   | 12        |
| 1.1.3.1 Aluminum alloys  | 13        |
| 1.1.4 Noble metals – Ag, Au, Ru, Rh, Pd, Os, Ir, Pt                        | 16        |
| 1.2 Materials for contacts   | 17        |
| 1.2.1 Requirements   | 17        |
| 1.2.2 Materials used for contacts  | 18        |
| <b>2. SPECIAL CONDUCTIVE MATERIALS</b>                                     | <b>23</b> |
| 2.1 Materials for resistors  | 23        |
| 2.1.1 Resistance materials for measuring devices                           | 23        |
| 2.1.2 Resistance materials for heating devices                             | 25        |
| 2.1.3 Non-metallic resistance materials                                    | 26        |
| 2.1.4 Electrical engineering components utilizing the resistance materials | 27        |
| 2.2 Materials for thermoelectric transformation                            | 28        |
| 2.2.1 Theory of thermo-electricity   | 28        |
| 2.2.2 Metals and alloys used for thermoelectric couple fabrication         | 30        |
| 2.2.3 Construction design of thermocouples                                 | 31        |
| 2.2.4 Semiconductor thermoelectric converters                              | 32        |
| 2.3 Solder materials   | 34        |
| 2.3.1 Low-melting solders  | 35        |
| 2.3.2 Soft solders   | 36        |
| 2.3.3 Hard solders   | 39        |
| 2.4 Materials for fuses  | 40        |
| 2.5 Metals and alloys for bimetals   | 41        |
| 2.6 Metals and alloys for electro-vacuum devices                           | 43        |
| <b>3. SUPERCONDUCTORS</b>  | <b>45</b> |
| 3.1 Examples of superconductor Applications                                | 46        |
| 3.2 Theory of superconductivity  | 47        |
| 3.3 Low-temperature superconductive materials                              | 49        |
| 3.4 High-temperature superconductors                                       | 51        |
| <b>4. MAGNETIC MATERIALS</b>   | <b>55</b> |
| 4.1 Physical principle of magnetism  | 55        |
| 4.2 Magnetic materials - properties  | 55        |
| 4.3 Ferromagnetic materials  | 58        |
| 4.4 Classification of magnetic materials                                   | 59        |
| 4.4.1 Magnetic soft materials  | 60        |
| 4.4.2 Magnetic metallic glass  | 62        |
| 4.4.3 Hard magnetic materials  | 64        |
| 4.5 Oxide magnetic materials   | 69        |

|   |            |
|---|------------|
| <b>5. HIGH PURITY MATERIALS</b>   | <b>75</b>  |
| 5.1 Distribution coefficient in crystallisation   | 77         |
| 5.2 Refining crystallization methods  | 79         |
| 5.2.1 Directional crystallization   | 79         |
| 5.2.2 Zone melting  | 80         |
| 5.3 Crystallization methods of refining and production of single crystals of metals, alloys and special materials | 82         |
| 5.3.1 General classification  | 82         |
| 5.3.2 Bridgman method   | 83         |
| 5.3.3 Drawing the crystal from the melt - Czochralski method of single crystal preparation                        | 84         |
| 5.3.4 Zone melting methods  | 86         |
| 5.3.5 Special crystallization technologies  | 88         |
| 5.4 Epitaxial technology  | 90         |
| 5.5 Diffusion   | 96         |
| 5.6 Metal deposition, sputtering and ion implantation   | 99         |
| <br>  |            |
| <b>6. SEMICONDUCTIVE MATERIALS</b>  | <b>102</b> |
| 6.1 Semiconductor material structure and atomic bond  | 102        |
| 6.2 Semiconductor conductivity  | 104        |
| 6.3 Semiconductive materials – basic classification   | 107        |
| 6.3.1 Elementary semiconductors   | 107        |
| 6.3.2 Compound semiconductors   | 109        |
| 6.4 Hall effect   | 114        |
| 6.5 Integrated circuit production technology  | 115        |
| 6.5.1 Fabrication and modification of Si wafers   | 115        |
| 6.5.2 Planar epitaxial technology of integrated circuit production  | 117        |
| <br>  |            |
| <b>7. OPTOELECTRONICS AND SPECIAL MATERIALS</b>   | <b>119</b> |
| 7.1 Optoelectronic systems  | 119        |
| 7.1.1 Electromagnetic radiation generators  | 119        |
| 7.1.2 Photo-detectors   | 122        |
| 7.1.3 Materials for wave- and light-guides  | 123        |
| 7.2 Materials for memory modules  | 126        |
| 7.3 Materials for photovoltaic (solar) cells  | 127        |
| 7.4 Liquid crystals   | 128        |
| 7.5 Ferroelectric materials   | 130        |
| 7.5.1 Piezo-electrics   | 132        |
| <br>  |            |
| <b>8. INSULATORS</b>  | <b>134</b> |
| 8.1 Attributes of insulators and dielectrics  | 134        |
| 8.2 Polarization of dielectrics and their properties  | 134        |
| 8.3 Gaseous insulators  | 138        |
| 8.4 Liquid insulators   | 140        |
| 8.5 Solid insulators  | 141        |
| 8.5.1 Solid inorganic insulators  | 141        |
| 8.5.2 Solid organic insulators  | 144        |
| 8.6 Dielectrics and capacitors  | 149        |
| <br>  |            |
| <b>LITERATURE</b>   | <b>151</b> |

# 1. CONDUCTIVE MATERIALS

## 1.1 HIGHLY CONDUCTIVE MATERIALS FOR ELECTRICAL ENGINEERING

Material properties are determined by the structure of the outer electron shell of the elements which the material consists of. If the atoms are close enough, their electrons from outer shell interact and this constitutes the atomic bond. Character and intensity of this bond is determined by the distribution of atoms in the space and this also determines the characteristic properties of the material. **Metallic materials are characterized by so called metallic bond** (electron bond). The metal can be visualized as a system of cations arranged in crystallographic lattice and surrounded by valence electrons which can be easily separated from the atom. Transfer of these valence electrons from atom to another facilitates the bond between atoms, cations are surrounded by a cloud of delocalized electrons which also provide balance to the repulsive force between cations. Present free electrons are the reason for **high thermal and electric conductivity of metals**.

Lowering the distance between two atoms eventually results in doubling of allowed bands which is facilitated by interaction by the two atoms. The distances between singular atoms in the crystal lattice are very small so all atoms interact with each others. Individual allowed bands disperse into multiple allowed bands which alternate with the band gaps. The bands of outer orbital electrons are dispersed first, the inner ones later. This is caused by inner orbitals being shielded by the outer orbitals. Electrons from the outer shell orbitals are more tightly bonded to the atomic core and therefore they disperse minimally and form fully occupied orbitals. Valence orbitals electrons are only weakly bonded with the atomic core and they interact during electric and chemical processes.

Electrons moving through the crystal lattice have both corpuscular and wave character and their energy disperse because of the oscillation of lattice ions, so their mean free paths are constricted. Higher oscillation of the crystal lattice results in more interactions between electrons and the lattice – this disrupts the flow of electrons in electric field and therefore facilitates **increase the electrical resistance of metals with increasing temperature**. The electrical resistance is also affected by character and perfection of the crystal lattice (lattice defects and additives), those change the electron mean free path.

### **Basic classification of conductors:**

**Solids:** metals and alloys.  
**Liquids:** mercury, melted metals, electrolytes.  
**Gasses:** ionized gasses.

Conductors **resistivity (specific electrical resistance)** is usually in range of  $\rho = 10^{-6}$  to  $10^{-2} \Omega\text{cm}$ . There are two different kinds of electrical conductivity: electron conductivity and ionic conductivity. Electrical current in the first type is facilitated by flow of electrons, as in metals and alloys. The mechanism in the second type creates the current by the transport of ions of the conductor material. Electrolytes are the prime example.

For the transport of electrical energy and construction of electrical circuits, the materials with conductivity provided by free electrons are used almost exclusively. Basic active materials used in electrical engineering for electricity conduction are specific non-ferrous materials and their alloys. These materials also have specific properties based on their structure which in solid state describe their difference from non-metallic materials.

### **Basic properties of conductive materials:**

- good electrical conductivity, low resistivity,
- good thermal conductivity,
- good mechanical properties along with high strength and plastic formability,
- thermoelectric properties.

Two large groups are defined by the purpose of the conductive material:

- **materials with high electrical conductivity** which are used as conducting material for coil wiring of electrical devices, exterior and cable lines etc. Silver has the lowest resistivity, however common conducting lines are made of copper Cu or aluminum Al. Copper has higher conductivity than Al, but the disadvantages are high density, low strength and troublesome availability.
- **materials with high electrical resistance** used as resistance materials for measuring equipments, resistors, heating elements, bulb wires etc. Best fitting materials for this purpose are alloys of certain metals, primarily copper, such as constantan, manganin, nickelin or even other metals, such as nichrome. Apart from previously

mentioned high resistivity, the resistance materials have to have low temperature coefficient of electrical resistance, low thermal expansion coefficient, sufficient strength at high operating temperatures.

Besides the two basic groups of conductive materials, there is another group of materials which are designed to fit the specific purpose or uncommon working conditions. For example materials for electrical contacts, thermocouples, materials for vacuum electrical engineering, high-purity metals for superconductors, bimetals and others.

**Basic electrical conducting metals are**

- copper and its alloys,
- aluminum and its alloys,
- noble metals.

## 1.1.1 COPPER - Cu

### Copper properties

Copper is reddish metal **with good hot and cold-formability**. It has an **excellent electrical and thermal conductivity** – Table 1.1. These properties however deteriorate quickly with impurities content. The impurities, for example Fe, Si, P, O (in form of  $\text{Cu}_2\text{O}$ ) strongly affect the conductivity of copper – Fig. 1.1. Copper is highly corrosion resistant in atmospheric environment, it has good **solderability** at both high and low-temperature and is part of many soldering alloys. It has relatively **good weldability**, problems are caused by its high thermal conductivity. These properties are also common for copper alloys. Copper is easily **degassed** and is therefore suitable construction material for electro-vacuum equipments. It has favorable mechanical properties, good machinability (forming, cutting). Its low melting point needs to be taken into account. Over 300 °C (**lower limit of recrystallization**) copper softens and loses its mechanical strength. For its high thermal expansivity it is not suitable for **glass-to-metal seals**.

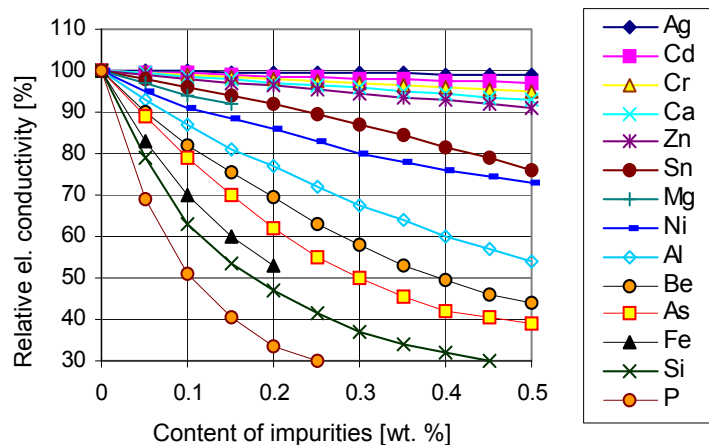
Another disadvantage of copper is its **brittleness** caused by annealing in hydrogen atmosphere. However this is necessary for production of electro-vacuum parts; degassing after annealing is therefore necessary. This embrittlement of copper is generally called **hydrogen disease** ( $\text{Cu}_2\text{O} + \text{H}_2 \rightarrow 2 \text{Cu} + \text{H}_2\text{O}$ ).

**Copper advantages** – excellent electrical and thermal conductivity!

**Standard of electric conductivity** ~ 58 MS/m (mega Siemens), i.e. resistivity of 0.0172  $\mu\Omega\text{m}$

**Table 1.1** Relative electrical and thermal conductivity of technically pure copper (20 °C)

| Metal     | Relative electrical conductivity [%]<br>(Cu = 100%) | Relative thermal conductivity [%]<br>(Cu = 100%) |
|-----------|---|--|
| Ag        | 106   | 108  |
| <b>Cu</b> | <b>100</b>  | <b>100</b>                                       |
| Au        | 72  | 76   |
| Al        | 65  | 56   |
| Mg        | 39  | 41   |
| Zn        | 29  | 29   |
| Fe        | 17  | 19   |
| Pt        | 16  | 18   |
| Sn        | 15  | 17   |
| Pb        | 8   | 9  |
| Ti        | 4   | 4  |



**Fig. 1.1** Effect of alloying elements on relative electrical conductivity  $\gamma$  of copper ( $\gamma$  of pure Cu = 100 %).

Table 1.2 lists the basic types of copper for electrical engineering applications (conductive materials), thermal application, mechanical engineering, vacuum equipments etc.

**Table 1.2** Conductive and metallurgical types of copper

| Description (purity levels)   | Semi-finished product:  |
|---|---|
| <i>Conducting types of copper:</i>                                    |   |
| copper 99.97 without oxygen   | strips, rods, tubes; use: vacuum applications                                     |
| copper 99.9 - copper ECu (electricity conducting)                     | wire, overhead lines, sheets, strips, anodes, dynamo bands, rods, profiles, tubes |
| copper 99.95 - copper ECu (electricity conducting) for advanced use   | wire  |
| copper ECu - Ag 0.1 (electricity conducting) contains up to 0.13 % Ag | dynamo sheets, lamellar rods  |
| copper ECu – 99.85  | wire  |
| copper cathodes Cu 99.95  | cathodes for vacuum applications  |
| copper cathodes Cu 99.9   | cathodes for casting semi-finished products and for special alloys                |
| copper for electricity conduction ECu                                 | casts, for example slip rings, contact segments                                   |

### **Copper ECu (conductive)**

ECu is the basic material for production of copper [conductors and cables](#).

#### **Classification of copper by mechanical properties:**

- 1) **soft:** (ultimate tensile strength  $R_m$  – min. 200 MPa but less than 300 MPa, ductility 10 to 35 %), copper is workable, isn't flexible.  
*use:* coil wiring, structure installations, power and data cables.
- 2) **medium:** ( $R_m$  - 290 to 370 MPa, ductility 3 %), slightly flexible.  
*use:* secondary distribution networks, rotor wiring of turbo-alternators.
- 3) **rigid:** ( $R_m$  - min 370 MPa, ductility 0.8 to 1.8 %), strong flexibility.  
*use:* in form of rope for exterior conduction, in form of sheets for knife switches.

### **Copper with reduced oxygen content - labeled Cu OFHC (Oxygen Free High Conductivity)**

Reduced oxygen content is achieved by melting and casting in vacuum or protective atmosphere. Oxygen content is held under 0.003 %. This material does not suffer from the hydrogen disease and is utilized in [magnetrons](#) and in [cathode X-ray tubes](#).

### **High purity copper (99.999 % Cu)**

Main alloying element is silver. It is used for [connection of hybrid integrated circuits, production of targets and for sputtering alloys](#).

## **USE OF COPPER IN ELECTRICAL ENGINEERING**

In electrical engineering, copper is used for [electric power distribution](#) in overhead wires and as [conductive core of cables and conductors](#). With regard to the copper prices increase, it is often replaced by aluminum. Copper is the preferred choice for wire and [foil conductor](#) (the plates of the printed board circuit) production. However, in microelectronics the wires are usually made of gold or AlSi alloy. Copper is also frequently used in [alloys for contact production](#).

Copper semi-finished products for electrical engineering are usually fabricated from cathodes of electrolytically refined copper. For [production of power cables, electrode copper](#) (ECu) is preferred; primary properties are **high electrical conductivity and simplicity of fabrication**. Parts used in electro vacuum industry are fabricated from copper with reduced oxygen content. It is produced by melting and casting in vacuum or protective atmosphere. This material does not become brittle in hydrogen atmosphere – does not suffer from the „hydrogen disease“.

Copper wires for [wire conductors and cables with rubber insulation](#) are tin-coated – this hinders the corrosive effect of sulfur which added to rubber as a vulcanizing agent. For contacts in high power hybrid integrated circuits, the [micro wires coated with aluminum](#) are used. Copper core constitutes the thermal and electrical conductor and the aluminum cover functions as the connection agent.

## 1.1.2 Copper alloys

Copper creates various alloys with noble metals, also with nickel, cobalt and manganese. Copper alloyed with certain amount of other metals forms brittle compounds. These are for example zinc, tin, silicon, magnesium, cadmium, antimony and others. Copper alloys have **more advantageous properties** than pure copper. They have **better mechanical properties**, **better corrosion resistance** and some can be **thermally hardened**. These alloys are used in electrical engineering for **contacts, springs, transistors and integrated circuits saddles and also for production of diamagnetic alloys**.

### 1.1.2.1 Copper-zinc alloys

**Brass** is alloy of **copper and zinc** - the zinc content ranges from 5 to 44 wt. %. If the brass consists only of copper and zinc, it is called binary brass. In practice, various other elements are commonly added (alloyed brasses) which enhance or otherwise change the brass properties. The commonly used additive is **lead** which, in the amount of around 3 wt. %, enhances machinability (machining brass) and improves the high-temperature malleability. Other metal additives are **aluminum** (corrosion resistance), **silicon** (fluidity of solders), **manganese** (abrasive properties) etc. Brasses are being extensively used for their good formability, machinability, corrosion resistance, color, also because their surface can be ground, polished and sanded, for their good fluidity during soldering and relatively favorable price. About 25 % of all copper production along with other alloying elements is used for brass production. The basic type of brass is the binary Cu-Zn system with quite complex phase diagram – see Fig. 1.2.

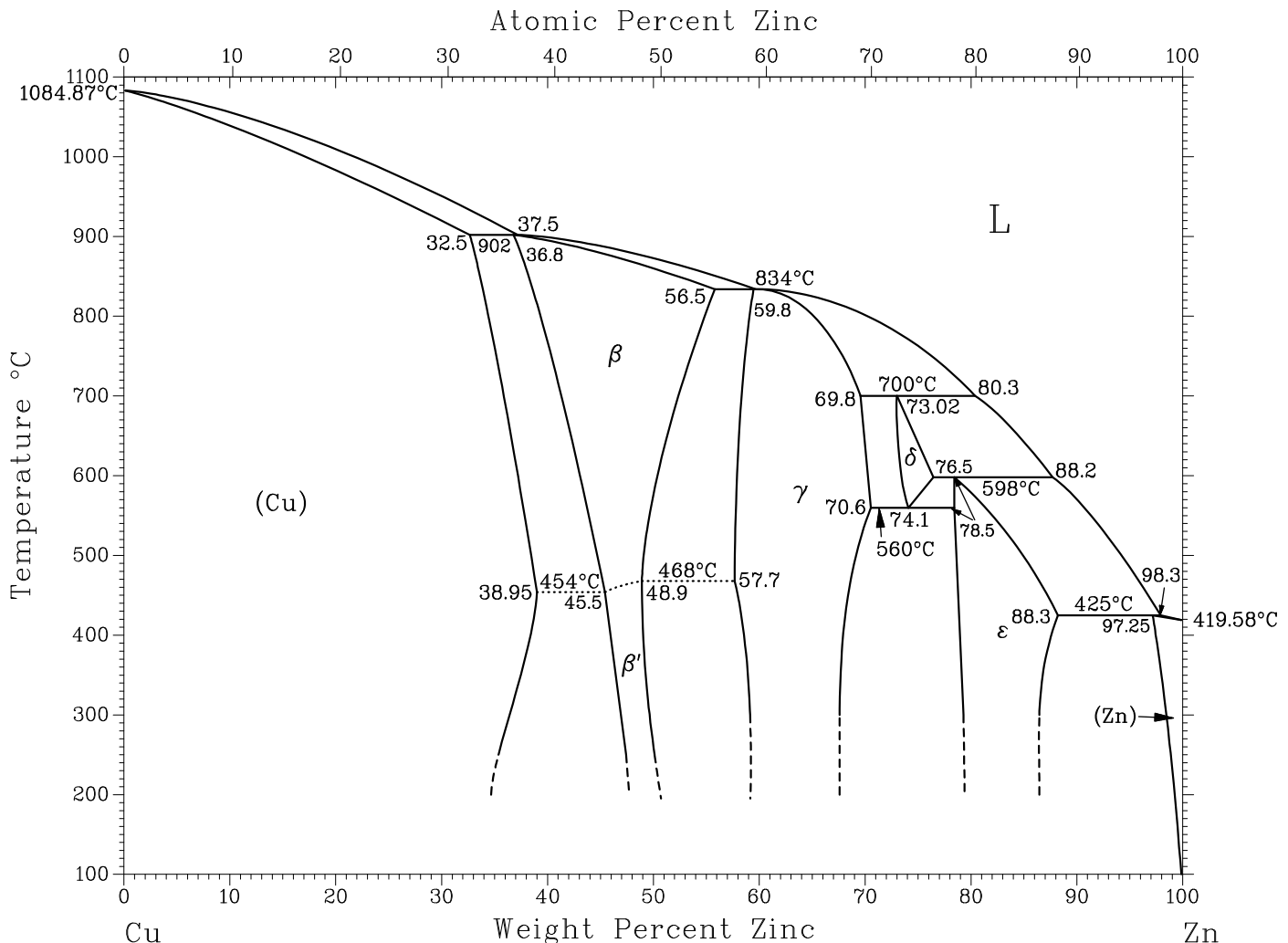


Fig. 1.2 Copper – zinc binary phase diagram (by Massalski, 1998)

The  $\alpha$  copper solid solution structure is stable up to 38 wt. % Zn (at about 454 °C), and this amount of zinc can be kept in metastable solid solution by rapid cooling to the room temperature.  $\alpha$ -brass exhibits decrease of formability in the temperature range 300 to 700 °C. This is why they are usually cold-worked.

Alloys with higher zinc content are usually heterogeneous, their structure contains, apart from the  $\alpha$  grains, also the  $\beta'$  phase (ordered solid solution). This hard and brittle phase transforms during heat treatment to  $\beta$  phase (non-uniform solid solution) with better formability, so the heterogeneous brass can be hot-worked up to cca 700 °C. Ductility reaches maximum value at solubility limit of Zn in  $\alpha$  copper solid solution, i.e. at 32 wt. % Zn. At higher Zn concentrations, the  $\beta'$  phase begins to form and the formability decreases. The alloy strength increases up to 45 wt. % of Zn, where the  $\beta'$  phase presents the majority of the structure. Brasses with more than 45 wt. % Zn have no practical use.

### Classification of brasses:

a) **Brasses for forming** contain from 5 to 42 wt. % Zn and can be both homogenous and heterogenous. They are labeled with the **Ms label** with added number which states the **copper content**. They are fabricated as semi-finished products (strips, sheets, rods, wires, tubes) and in soft (annealed), medium, rigid or spring-rigid state.

**Tombac (pinchbeck)** is Cu-Zn alloys with **copper content higher than 80 wt. % Cu** (Ms 96 to Ms 80). These alloys have good resistance against atmospheric corrosion and good low temperature formability. They are mostly produced in form of strips and sheets for pressing, drawing and minting. They are used as components for **electrical engineering**, for pressure gauges, corrugated tubes, membranes, sieves. Other use: coins, plaques.

**Single-phase brasses**  $\alpha$  brasses are mostly utilized in the form of sheets, strips or wires. Their strength and ductility increases with zinc content; the brasses Ms 70 and Ms 67 have optimal cold working properties.

**Two-phase brasses**  $\alpha+\beta'$  brasses form when the solubility limit of zinc in copper solid solution is exceeded. Most common alloys are Ms 63, Ms 60 and Ms 58 for forgings. Addition of 1 ÷ 2 wt. % Pb enhances their machinability. The disadvantage of two-phase brasses is their tendency to stress-corrosion cracking, also called “seasonal cracking”. Internally stressed parts, exposed to corrosive environment, especially ammonium, can crack even without external load, e.g. during storage. To remove the internal stress, given parts needs to be annealed at 250 to 350 °C.

b) **Brasses for casting** commonly contain between 58 and 63 wt. % Cu. Their structure is heterogeneous  $\alpha+\beta'$ . They typically have good fluidity and low tendency to segregation. Their machinability can be enhanced by lead addition (1 ÷ 3 wt. %).

Certain types of brasses with melting point over 500 °C belong to the group of so called **hard solders (brazing metals)**, used for metal parts joining.

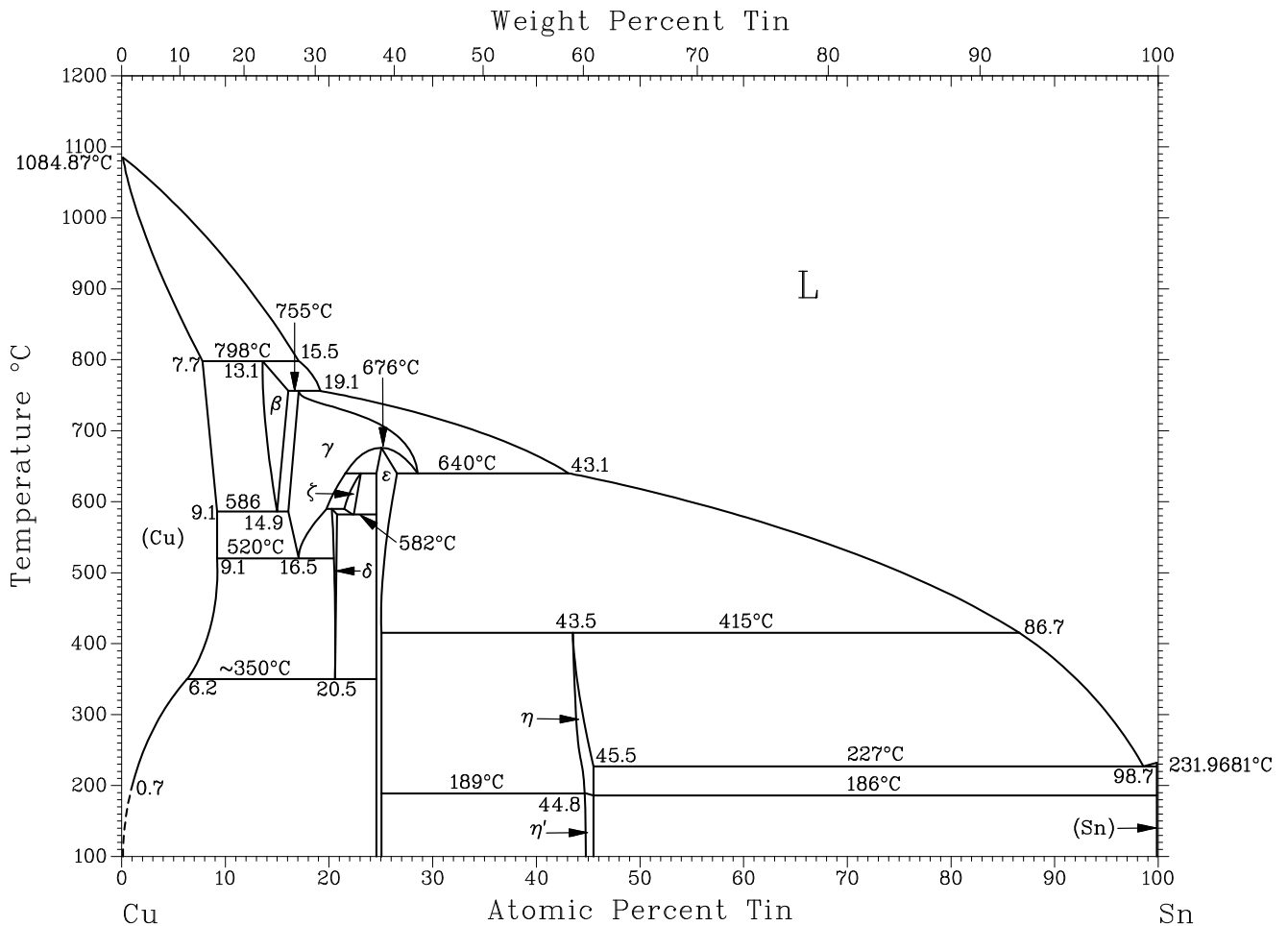
The **brass hard solders with silver** are more expensive, have lower melting points and if the content of silver exceeds 50 wt. %, they are referred to as silver alloys or silver solders.

### 1.1.2.2 Copper tin alloys

**Bronze** is alloy of **copper and tin or other elements**. Bronzes are generally copper alloys with the exception of brasses. Bronze type is therefore labeled according to its main alloying element (e.g. **tin bronze, aluminum bronze, lead bronze, nickel bronze, manganese bronze**). Bronze is used in all applications requiring **higher tensile strength  $R_m$  and corrosion resistance** than brasses can achieve.

The oldest bronze type is the tin bronze. Equilibrium binary diagram copper-tin (see Fig. 1.3) shows large number of phases. At room temperature,  $\epsilon$  (36.5 ÷ 38 wt. % Sn) and  $\eta'$  (~ 61 wt. % Sn) phases are stable.  $\eta$ ,  $\zeta$ ,  $\delta$ ,  $\gamma$  a  $\beta$  phases are stable at higher temperatures. The Cu-Sn alloy does not reach equilibrium structure at normal cooling rates. The reason for this is the strong segregation of tin during bronze solidification and very slow diffusion of tin at low temperatures.





**Fig. 1.3** Copper – tin binary phase diagram (by Massalski, 1998)

**Tin bronzes for forming** are usually homogenous with tin content up to 9 wt. %, with solid solution structure. Effect of tin on bronze properties is similar to effect of zinc in brasses - it enhances their mechanical properties. Tin improves chemical stability of copper, its hardness and strength but it deteriorates its electrical and thermal conductivity. Bronze for electrical engineering is mainly produced in soft form. Maximum strength is reached at around 20 wt. % Sn, maximum ductility at about 5 wt. % Sn. Formed tin bronzes have higher strength and corrosion resistance than brasses. Higher tin content improves sliding properties (to 9 wt. %) which is utilized in heavy ball bearings. In hard state, brass is viable choice for **springs** working in corrosive environment. They are commercially available in form of sheets, stripes, wires, rods, tubes. Form: soft, medium, hard, spring hard.

**Table 1.3** Chemical composition and mechanical properties of tin bronzes for forming

| Alloy bronze  | Chemical composition [wt. %] |         |        |             | Mechanical properties in annealed state |                  |         |          |
|---------------|------------------------------|---------|--------|-------------|---|------------------|---------|----------|
|               | Sn                           | Pb max. | P max. | others max. | $R_m$ [MPa]                             | $R_{p0.2}$ [MPa] | $A$ [%] | $HB$ [-] |
| <b>Cu-Sn1</b> | 0.8÷2.0                      | -       | -      | 0.7         | 240                                     | 80               | 35      | 60÷80    |
| <b>Cu-Sn3</b> | 2.5÷4.0                      | -       | 0.3    | 0.7         | 280                                     | 100              | 40      | 60÷90    |
| <b>Cu-Sn6</b> | 5 ÷ 7                        | 0.05    | 0.255  | 0.4         | 350                                     | 150              | 40      | 70÷90    |
| <b>Cu-Sn8</b> | 7 ÷ 9                        | 0.05    | 0.25   | 0.4         | 380                                     | 200              | 50      | 80÷100   |

**Tin bronzes for castings** are used more commonly than bronzes for forming. They usually contain 10 to 12 wt. % Sn, they have heterogeneous structure consisting of  $\alpha$  grains and  $(\alpha+\delta)$  eutectoid solution. They have good strength and toughness, high corrosion resistance and excellent sliding properties provided by stiff eutectoid  $(\alpha+\delta)$  and soft  $\alpha$  phase in the structure. They have low shrinkage coefficient  $\sim 1\%$  (brasses 1.5 %) but worse flow properties than brasses. They suffer from dendritic segregation and micro-porosity of the casts (achieving pore-less casting is problematic). Expensive bronzes with higher tin content are nowadays used almost exclusively for specific type of casts. Table 1.3 shows typical characteristics of common tin bronzes after casting.

**Table 1.4** Chemical composition and mechanical properties of tin bronzes for castings

| Alloy bronze        | Chemical composition [wt. %] |           |          |         | Mechanical properties |                     |            |             |
|---------------------|------------------------------|-----------|----------|---------|-----------------------|---------------------|------------|-------------|
|                     | Sn                           | P         | Pb       | Ni      | $R_m$<br>[MPa]        | $R_{p0.2}$<br>[MPa] | $A$<br>[%] | $HB$<br>[-] |
| <b>Cu-Sn1</b>       | 0.5÷1.0                      | -         | -        | -       | -                     | -                   | -          | -           |
| <b>Cu-Sn5</b>       | 4 ÷ 6                        | max. 0.1  | max. 0.2 | 0.2     | 180                   | -                   | 15         | 50          |
| <b>Cu-Sn10</b>      | 9.5 ÷ 11                     | max. 0.3  | max. 0.5 | 1.5     | 220                   | 160                 | 15         | 60          |
| <b>Cu-Sn12</b>      | 11.5 ÷ 13                    | max. 0.05 | 0.5      | 1.5     | 240                   | -                   | 8          | 80          |
| <b>Cu-Sn10-P1</b>   | 9.5 ÷ 11                     | 0.4÷1.0   | max. 0.3 | -       | 220                   | -                   | 3          | 80          |
| <b>Cu-Sn10-Pb5</b>  | 9.5 ÷ 11                     | max. 0.07 | 4 ÷ 6    | 0.5÷1.5 | 200                   | 160                 | 12         | 65          |
| <b>Cu-Sn10-Pb10</b> | 9.5 ÷ 11                     | 0.05      | 9 ÷ 11   | 0.3÷1.0 | 170                   | -                   | 6          | 60          |

## Special bronzes

Tin in special bronzes is partially or completely replaced by other elements which are also used to differentiate the kind. Based on their structure and related properties and also by the manufacturing process, they are divided in two different groups – bronzes for forming and bronzes for casting.

### Red bronzes

are ternary Cu-Sn-Zn alloys. Some are also alloyed with low amounts of lead. They have good machinability and their surface can be easily polished. These are cheaper, thanks to the lower content of tin, compared to the binary Cu-Sn bronzes. Common application includes armatures casts, pump parts etc. They have similar composition as bronzes for sculptures – the content of zinc is often much higher than tin content.

### Aluminum bronzes

are Cu-Al alloys, possibly with another metal. They contain up to 12 wt. % Al. Bronzes with higher Al content suffer from unfavorable brittleness. Aluminum bronzes are characteristic for their good heat resistance up to 800 °C and high corrosion and fatigue resistance (even corrosion fatigue). They are also very hard, have high abrasion resistance and good sliding properties. This material is suitable for memorial tablets, welding jaws, furnace electric contact clamps worm wheels, armatures, valve seats, ball bearing for high pressure and slow speed applications.

### Silicon bronzes

They are used as a replacement for costly tin bronzes. Cu + Si alloys (usually **3 to 4 % Si**) have better mechanical properties than tin bronzes and also good fluidity. Primary crystallization occurs in wide temperature range  $\Rightarrow$  segregation tendency, non-equilibrium crystallization (rapid cooling)  $\Rightarrow$  heterogenous structure. Good high and low formability  $\Rightarrow$  used for drawing and minting. These alloys have higher strength and can be used in wider temperature range (-180 up to +200 °C). The hardness and strength can be improved by manganese, nickel or zinc. Relatively bad machinability can be enhanced by lead (0.5 wt. % Pb). Alloys for forming contain up to 3.5 wt. % Si, the alloys for casting up to 5 wt. % Si.

### Phosphor bronze

Alloy CuP8 is used for brazing. The structure is eutectic and the alloy has an excellent fluidity. However, the solder joints are brittle and cannot be used to brazing of steels or any mechanically strained parts, especially with dynamic loading.

### Beryllium bronze

belongs to the group of thermally hardenable copper alloys and it can reach the highest strength of all copper materials. Addition of beryllium is around **1 - 2 wt. %**. 2 wt. % is an optimum which, after thermal hardening, can provide ultimate tensile strength of 1400 MPa and 400 *HV* hardness. Beryllium bronzes exhibit **excellent spring properties**, best outside the non-ferrous alloys group. They maintain their high tensile strength even after prolonged high-temperature exposure.

**Beryllium bronze foils.** Beryllium bronze can be rolled to very thin foils – up to 1.4  $\mu\text{m}$  while maintaining reasonable strength. It is often used as nonmagnetic insulation in recording heads for media recording.

**Beryllium bronzes with addition of Ni, Co, Mn, Ti.** They have (apart from excellent mechanical properties) a good corrosion resistance. These alloys are used for production of **springs with good electric conductivity, non-sparking tools** for mining applications and chemical industry, **swaging for forming, ball bearings for large loads and high radial speeds** (superb friction properties).

### Leaded bronze

is a mixture of copper and lead (alternatively Sn) grains – their mutual solubility in solid state is very low, slightly higher in liquid phase. Lead content is in range 10 to 30 wt. %. In case of fine distribution and small grain size of both phases using either rapid cooling or powder metallurgy, the lead bronze has **good sliding properties** and good **thermal conductivity** which is viable for steel saddles of friction bearing, designed for high specific pressures, high radial speed and high working temperatures (300 ÷ 320 °C), e.g. ball bearings of car engines, compressors, train cars; ternary alloying elements Ni, Zn, Mn or Ag decrease the segregation and refine the grain.

**Note:** The content (concentration) of alloying elements will be in the next text used only in % (it means in wt. %).

## 1.1.2.3 Special copper alloys

### Alloys with high machinability

Commonly called machining brass (or bronze) since they are produced with machine tools (turning lathe, milling machine). Splinter forming during machining is required not to be continual but to break into smaller pieces. This is achieved by lead addition. They are used in electric contacts and connectors production etc.

#### Cu-Co alloys

is copper alloyed with Co and P. Thus alloyed material maintains its high electrical and especially thermal conductivity. The hardness is stable even after thermal exposure. It is used in electrical engineering in form of strips as and precursor for transistors saddles, for integrated circuits, switches, plugs and others.

#### Cu-Fe alloys

Suitable treatment can substantially enhance mechanical properties of primary copper. Alloy is called *Olin brass*. Often replaces tin brass as it is cheaper.

#### Cu-Ni-Sn alloys

These alloys are specifically designed for the production of inputs of passive electronic devices. Their characteristic property is high oxidation resistance – they are used for outputs of devices not affected by their lower electrical conductivity, wall sockets, electrical contacts etc.

### Nickel and manganese bronze

They are typically based on ternary Cu-Ni-Mn system also alloyed with low amounts of Si, Al and Fe. Alloys with 15 to 20 % Ni have good low temperature formability with only low strengthening, suitable for highly corrosive environments and operation at elevated temperatures. Bronze with 25 % Ni is used as coin material. Higher amount of Ni (30 %) further increases its corrosion resistance and it is the material for chemical and pharmaceutical industry, as well as for medical tools and instruments. Alloys with 44 % Ni are suitable for thermocouple production (used up to 600 °C). Resistant alloys for resistors of measuring and controller instruments are another kind of bronze of this group. One of such is alloy Cu-Ni30-Mn2 named *nickelin* (up to 400 °C), alloy Cu-Ni45-Mn, so called *constantan* (up to 500 °C), and resistance alloy Cu-Ni3-Mn13 known as *manganin* (up to 200 °C).

Magnetic hard material for permanent magnets is alloys **Cu-Ni-Fe** and **Cu-Ni-Co**. They can be cold-formed.

Alloys **Cu-Ni-Fe-Mn** can withstand even most severe corrosion environments, such as in condenser tubes for navy ships.

Alloys **Cu-Ni-Al** (e.g. Cu + 6 % Ni + 1 % Al) with good corrosion and oxidation resistance are especially suitable for spring manufacture.

### A. Nickel bronze

**Cu + Ni** exhibit perfect mutual solubility in both liquid and solid phases. Alloys with high Ni content are ferromagnetic.

**Cu + Ni** alloys have good strength at both normal and elevated temperatures and are also resistant against corrosion in electrical field and their **electrical resistance is only weakly affected by temperature changes**.

Ternary alloying elements: Mn, Fe, Al. Ternary alloys are hardenable.

**Constantan** (54 % Cu, 45 % Ni, 1 % Mn). This alloy has high **electrical resistance** and **low temperature coefficient of electrical resistance**, i.e. its resistivity is not strongly temperature dependent, also has good strength and it is resistant against stress corrosion cracking. Increase of the manganese content up to 1 % changes temperature coefficient of electrical resistance which is usually negative and not strongly temperature dependent.

Cu + 44 % Ni alloy has high thermoelectric voltage compared to Fe and Pt  $\Rightarrow$  material for iron–constantan thermocouples. Tensile strength is 400  $\div$  500 MPa. Constantan is, as **resistance material** used for fabrication of **thermally stable resistors**, also **thermocouples** (applicable up to 600 °C), **resistance sensors and wiring of commercial resistors**.

**Nickelin** (67 % Cu, 30 % Ni, 3 % Mn). By annealing, oxide layer with good insulation properties can be formed on the surface. Alloy tensile strength is about 350  $\div$  400 MPa. It is used for fabrication of **rheostats (variable resistors) for technical use, control resistor**, in case **stable resistance** is not required.

**Isotan** (55 % Cu, 44 % Ni, 2 % Mn). Tensile strength 450  $\div$  550 MPa. Mainly used for **resistor** fabrication.

### **B. Manganese bronze**

**Manganin** (86 % Cu, 12 % Mn, 2 % Ni). Its properties are not stable and the alloy is therefore thermally aged at elevated temperatures in several cycles. Ultimate tensile strength reaches 500  $\div$  550 MPa. Maximal operation temperature is 140 °C. Manganin is, as **resistive material**, used for production of **stable and precise resistors** produced from wires or sheets (manganin foil is glued on laminated paper from both sides and subsequently etched). Another use is manufacture of resistive pressure gauges which make use of the piezoelectric effect – changes in pressure are detected by changes in electrical resistance of the bronze.

**Zerinin** (87 % Cu, 7 % Mn). Very similar properties to manganin, but can also contain germanium. Tensile strength is of 350  $\div$  400 MPa. Used for production of **resistors with high accuracy**.

**Cast and formed alloys** – complex alloys with low concentrations of Ni, Si, Be, Al, Cr, Zr, Co, V, Fe.

Application: **welding electrodes, thermally stressed** aircraft parts.

**Application of some Cu alloys in power engineering**– summary:

**Beryllium bronzes** (2  $\div$  2.5 % Be), typically processed by water quenching from 800 °C, tempering at 250 to 350 °C, 2 to 3 hours. They have about 55 % electrical conductivity of Cu.  $\uparrow R_m$ ,  $\uparrow$  electrical conductivity.

Application: **heavily strained springs with electrical current flowing through them**.

**Electrical conductive bronzes**:  $\sim$  1.2  $\div$  1.5 % Sn  $\Rightarrow$  40  $\div$  50 % electrical conductivity of Cu.  $R_m \sim$  600  $\div$  700 MPa.

**Cu + 0.5  $\div$  1.5 % Cd**. Application: **very long-distance conduction, trolley wires, welding electrodes**.

**Cu +  $\sim$  0.1 % Ag**. Decreased conductivity by 0.7 % compared to pure Cu,  $\uparrow$  recrystallization temperature (300 °C).

Application: **rotor wiring in turbo alternators**.

**Cu + 0.5  $\div$  1 % Cr**. Application: electrodes in resistance welding devices.

**Cu + 0.3  $\div$  1 % Te**. Good machinability,  $\uparrow$  el. conductivity.

## **1.1.3 ALUMINUM - Al**

Development in production of high-purity aluminum allowed utilization of its **good electrical conductivity** which is about **65 % of copper**. Aluminum is therefore **amongst the top four metals with lowest electrical resistance** preceded by silver, gold and copper. Important areas of application are electrical engineering and microelectronics. Aluminum is commonly used for fabrication of **wires (external conductors, wiring, cables)** and **micro-wires**, its good formability at normal temperatures allows the production of various parts and casings (saddle washers). Dielectric properties of its oxides forming on the surface are utilized in production of **electrolytic capacitors**. Aluminum is often used as and coating materials, since the coating layers are easily produced by vapor deposition or sputtering, the coatings are also used as and **reflector** in black-and-white or color TV screen and as conductive surface in **microelectronic parts**, for cast parts – **coolers** etc.

**Advantages** – Al is  $\sim$  3 times lighter than Cu; Al cable with the same electrical resistance weighs about half of the Cu cable; good corrosion resistance.

**Disadvantages** – low strength (the aluminum external conductor network needs to be combined with steel suspension ropes).

**Alloying and forming** cannot be used to improve its strength  $\Rightarrow$  lowers the electrical conductivity, low crystallization temperatures.

## Aluminum properties

Aluminum is silvery white, soft, malleable metal which, in aerial conditions, forms a thin layer of grey-white  $\text{Al}_2\text{O}_3$ . This layer is chemically stable and protects the base metal against corrosion. Aluminum has a low specific density ( $2.64$  to  $2.7 \text{ kg}\cdot\text{dm}^{-3}$  depending on the level of forming). It is quite soft, so it can be formed without chipping. Aluminum disadvantage is low creep resistance – causes deformation of the product. Aluminum parts have low mechanical strength. It can be increased by alloying or micro-alloying. As micro-alloying elements, beryllium in form of  $\text{AlBe}_5$  or boron, are often used. Alloying by Cu, Mg, Zn, Si, enhances its mechanical properties, but also worsens its chemical resistance. Welding is problematic due to the presence of a tough layer of oxide on the surface. Electrical conductivity is strongly affected by the aluminum purity.

**Corrosion resistance:** Al is stable in aerial conditions thanks to high  $\text{O}_2$  affinity of Al → forms thin layer of compact  $\text{Al}_2\text{O}_3$  which protects the metal against further oxidation → specific volume of  $\text{Al}_2\text{O}_3 = 1.28$  times higher than Al ⇒ highly protective. **Aluminum** is stable in neutral, weakly acidic and basic environments, is resistive in neutral and oxidative salt solutions.

### Electro conductive Al - EAl

- 1) *Cables for low, high and very high voltage conductive networks* – able to cool down faster and are also lighter than copper cables. Poor mechanical properties are compensated by steel support suspension.
- 2) *Cores of power cables*.
- 3) *Coil wiring of electrical devices* – transformers, squirrel cage rotors.
- 4) *Foils* – thickness of  $0.02$  to  $0.005 \text{ mm}$  for production of foil (EAl 99.5) and electrolytic capacitors (EAl 99.85).
- 5) *Construction material* – plates of rotary capacitors, heat sinks of semi-conductor components etc.

### Power wires and cables

Power wires and cables are used for electricity distribution. Wires have diameter of  $1.6 \div 13 \text{ mm}$ , in soft and semi-hard state up to  $4.5 \text{ mm}$ , and in all sizes in hard state.

### Power cables

PVC insulated cables – cables with aluminum core, PVC insulation and wire braiding.

Aluminum wire braids – used for overhead high voltage cables.

Aluminum strips – for distribution network connection.

Steel-aluminum conductors for exterior, high-voltage use have steel core surrounded by aluminum cover. The steel has tensile strength of  $1200 \text{ MPa}$  to ensure necessary mechanical strength, aluminum provides good electrical conductivity.

### Thin cables and micro-cables

Electro-conducting aluminum 99.5 % is not sufficiently pure for connection of microelectronic components. Therefore the 99.99 % pure aluminum is used. Because of its low strength, the minimum diameter is  $0.2 \text{ mm}$ . Lower diameter wires can be produced only from aluminum alloyed with silicon, magnesium or copper.

### Aluminum foils for electrolytic capacitors

They are used for production of electrolytic capacitors as anode and cathode foils. Higher specific surface and therefore higher capacity is achieved by chemical or electrochemical etching, nowadays in mixture of common salt and other compounds. Dielectric layer composes of aluminum oxide prepared by anodic oxidation of etched anodic foil.

## 1.1.3.1 Aluminum alloys

Based on their typical applications, the aluminum alloys are divided in two groups – aluminum alloys for casting and alloys for forming. From the metallurgical point of view, these alloys can be divided to hardenable and non-hardenable. The alloys for casting and forming are not easy to differentiate – some alloys for forming have good casting properties and also, some alloys for casting can be formed.

Basic alloys for casting are for example: Al-Si, Al-Si-Mg, Al-Cu, Al-Mg, Al-Si-Cu, less common are Al-Zn, Al-Zn-Mg, Al-Cu-Mg, alloys for piston casting belong to separate group.

Al-Mg, Al-Mn (non-hardenable), Al-Mg-Si, Al-Cu-Mg, Al-Zn-Mg (hardenable) are examples of alloys for forming.

### **1. Al – Si alloys (silumines)**

**Silumine** is the most common aluminum alloy for casting. It contains about 12 % Si, sometimes also alloys with Cu (1 %). The casting shapes can be quite complex with thin walls without danger of cracks formation. Specific density of  $2.65 \text{ kg/dm}^3$ , the castings are light, can be further machined, welded and have sufficient corrosion resistance. Also can be sand-cast, ingot-mold- and also pressure cast. These alloys are widely used in electrical engineering for construction parts production: **frames and end plates of engines, cases and frames of electromagnetic and measurement devices, cable connection covers** etc.

**2. Al – Ni alloys** are mostly used for poly-component systems operated at elevated temperatures.

**Ni** (up to  $\sim 2.5$  %) in some alloys enhances mechanical properties at normal and elevated temperatures and also improves corrosion resistance.

**3. Al – Zn alloys** have high strength, lower toughness, lower corrosion resistance and are more easily hot-formed.

**4. Al – Mg alloys.** Mg is added to most of the Al alloys. It enhances its hardening properties, increases corrosion resistance. Mg content in alloys for forming is up to  $\sim 8$  %; in the alloys for casting it is up to  $\sim 11$  %.

**5. Al – Mg – Mn alloys** have high strength, are plastic, easy to drawn, have good corrosion resistance. Mn enhances the hardening and has no significant effect on the structure.

**6. Duralumin (dural)** – thermally hardenable aluminum alloy Al-Cu-Mg-Mn with  $\sim 4$  % **Cu**,  $0.6$  % **Mg** and  $0.6$  % **Mn**. Hardened alloys have tensile strength  $R_m = 450$  to  $550$  MPa. They are used for production of formed semi-finished products. Alloy with higher magnesium (about  $1.2 \div 1.6$  %) and manganese content ( $\sim 1$  %).

**Super-duralumin** – has even higher tensile strength (more than  $550$  MPa). Duralumin alloys are used in wide range of **construction applications**.

**7. Aldrey alloy** – aluminum alloy for electro-conducting. The alloys consists of Al,  $0.5$  % **Si** and  $0.5$  % **Mg**. It has about double the tensile strengths of pure aluminum while keeping its good electrical conductivity. Thermal treatment and low-temperature forming enhances the tensile strength up to  $300$  MPa which is sufficient for production of **high-voltage power conductors**.

**8. Jereal alloy** – with increased (by about  $0.15$  %) content of Zn. Thermally treated wires reach strength of  $360$  MPa. Jereal can be used for **exterior network cables** and also for applications bellow  $80$  °C. Recrystallization caused by higher temperatures deteriorates its mechanical properties.

**9. Condal alloy** is aluminum alloy with  $0.4$  % **Mg** and  $0.4$  % **Fe**. It is suitable for **transformer wiring**, electrical **rotary devices** and any other applications where pure aluminum cannot be used due to limited mechanical properties.

**10. Al – Ni alloy** was a big achievement in the development of **magnetically hard materials**. It is alloyed with **Fe, Al, Ni** and has unusually viable magnetic properties. With the aluminum content of  $12$  to  $14$  %,  $24$  to  $28$  % Ni, (balance Fe) is the maximum energy product  $(BH)_{\max} = 5300 \text{ J/m}^3$  while  $B_r = 0,55$  to  $0,65$  T and  $H_c = 40000$  to  $51000$  A/m. To achieve such properties, the alloy needs to be thermally worked, rapidly cooled from  $1200$  to  $600$  °C, held at this temperature for several hours and then slowly cooled. Addition of cobalt, copper or titanium and cooling of the material in strong magnetic field can further enhance the properties of Al – Ni alloys. In such case, the correct label of the alloy is **Al – Ni – Co** (apart from **Fe**, the most important alloying elements are **Al, Ni, Co** which are the typical hard-ferromagnetic materials). Optimal properties are reached at  $8$  % Al,  $14$  % Ni,  $24$  % Co,  $3$  % Cu and balance of Fe. Thermal treatment consists of rapid cooling (quenching) from  $1300$  °C (from  $900$  °C in strong magnetic field) and hardening at around  $600$  °C. After this treatment, the alloy has  $B_r = 1$  to  $1.4$  T,  $H_c = 40000$  to  $52000$  A/m and  $(BH)_{\max} = 15000$  to  $22000 \text{ J/m}^3$ . The only disadvantage of Alnico magnets is their brittleness caused by their stiffness which makes the machining complicated. This is also true for Al – Ni alloys. Low machinability along with low dimensional accuracy and brittleness of cast magnets forced the magnet manufacturers to look for different technology – powder metallurgy. Metal powders prepared by grinding are pressed into desired shape and annealed at  $1300$  °C. Alni and Alnico magnets produced by this process have magnetic properties comparable to the cast material but also have higher strength, are not brittle and have better machinability. The application range is very wide,  $80$  % of all hard ferromagnetic materials is used for **permanent magnets**.

## Micro-wires

**AlSi1 micro-wire** is mass produced and it is after the golden micro-wire the second most utilized material in microelectronics. Ultrasound soldering is used to join this alloy with other metals. During this process the layer of oxides is removed at elevated temperature. The metallurgical connection between the alloy and other metal is therefore created.

**AlCu4 micro-wire** has higher electrical conductivity (by about 15 %) than AlSi1. It is used as joining wire for power transistors and micro circuits.

**Copper wire and micro-wire plated with aluminum** – produced in diameter range of 25  $\mu\text{m}$  up to 2÷3 mm. Copper core provides good electrical and thermal conductivity, aluminum plating is used to join with other component. Similar used as AlCu4 wire.

## Al powder metallurgy

**Sintered Aluminum Powder** is special product used for production of pressed, rolled, forged and other sintered semi-finished products from both pure aluminum and its alloys.

## Aluminum conductors

The term „aluminum conductors for electrical engineering” is used for production of conductors with aluminum core which must fulfil requirements given by both standards and operation demands. Important attributes of aluminum wires are: outer diameter, tensile strength, ductility, bend fatigue resistance and electrical resistance. 99.5 % aluminum (EA1 99.5) is the precursor for conductor production. Main impurities are Fe, Si, Cu, Mn, Mg, Zn.

### Al wire production technology:

Aluminum wire can be produced by three different technologies:

- Rolling.
- Pressing.
- Continual forming of rolled wire at elevated temperature.

### Cold wire drawing of aluminum and its alloys

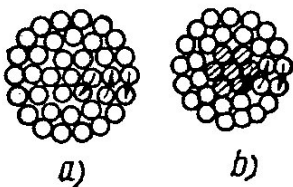
Aluminum wires drawn at normal temperature are produced from both pure aluminum and its alloys. Wire product categories are: round wired with normal precision, precise round wires, rivet round wires, square and hexagonal wires. Wires rolled at elevated temperature or extruded wires are the precursors for the cold-formed aluminum wires.

### Aluminum cables production

AlFe cables are used as the exterior overhead distribution network. AlFe cables consist of steel core wire or rope with 1 to 4 layers of outer shell from aluminum wire. For example: the exterior 220 kV high-voltage distribution network uses AlFe 450/52 rope (i.e. approximately: Al = 450  $\text{mm}^2$ , Fe = 52  $\text{mm}^2$ ).

Aluminum wires for distribution network are divided in two groups; common aluminum cables and aluminum cables with steel core – Fig. 1.4. Common aluminum cables are fabricated from 1.7 to 3.55 mm diameter wire with one up to three layers – on cable therefore consist of 7, 9 and 37 wires. Aluminum cables with steel core have the Al:Fe ratio of 3:1, 4:1, 6:1 and 8:1. Steel core can consist of one, three, seven, twelve and nineteen wires.

Number of aluminum wires is between six and fifty-two. Wires are reeled in four layers around the steel core. The steel core in steel-aluminum cables can be also reeled around the base steel thread.



a) common b) with steel core

**Fig. 1.4** Aluminum cable

In electronics, aluminum is mostly used as high-voltage conductor. Aluminum conductor with similar electrical resistance as copper conductor has 1.3 larger diameter but weigh only about a half.

**Strength** of aluminum conductors is closely connected with creep – slow plastic deformation. To increase their mechanical strength, the cables with larger diameter have steel core. Low strength is problematic during short-circuiting of transformers and connection stations.

Aluminum is, compared to copper, very **soft**, the joining conductors must therefore be in certain size and shape to prevent damage of the joint. Thin conductors are prone to mechanical damage thus losing its function – e.g. slit in the conductor reduces its diameter and therefore also its conductivity and mechanical strength. Coating of aluminum conductor is therefore required since any damage to the surface can result in corrosion attack.

**Creep** – aluminum conductors need to be tight and protected against wire loosening. Loosening is caused by creep.

**Thermal expansivity** of aluminum is different from other metals and has favorable effect on joints. Movement of two adjacent metals removes the oxide layer on aluminum, practically lowering the contact resistance.

Correct surface treatment provides corrosion protection. Aluminum reacts with oxygen and quickly develops oxide film ( $\text{Al}_2\text{O}_3$ ) on its surface, this film is chemically stable. However the thermal and electrical conductivity is low which is usually undesirable, but in some cases, can be utilized as insulation layer.

#### **Surface chemical treatment:**

**Anodizing** – most common surface treatment: surface is electrically dissolved and transformed to aluminum oxide – this surface is porous, hard and low-conductive.

**Metallic coating:** protective layer must be non-porous and crack-less, well adherent to the conductor, with sufficient thickness and good mechanical properties.

**Thermal coating** – hot dipping in melted metals, by diffusion, metal vapors or gaseous metal compounds, amalgam.

**Electro-chemical coating:** without electrical current or with electrical current (galvanic). Solution containing the coating metal is decomposed by the electrolysis. The coating metal is connected as anode.

#### **Cathodic metal sputtering.**

**Mechanical coating:** metal spraying, plating.

**Varnish coating:** applied in several layers by either varnishing or spraying.

**Enameling:** Thin layer of boron-silicate glass. Formed coating is highly resistant against acids, but it is prone to mechanical impact damage and rapid temperature changes.

**Asphalt, tar and natural rubber coating:** viable and cheap protection against atmosphere, however light-deteriorated; applied in several layers with inserted fabric, paper etc. by dipping, spraying.

**Plastic coatings:** highly viable for use in chemical industry. Applied: by gluing, varnishing or pressing.

## **1.1.4 NOBLE METALS – Ag, Au, Ru, Rh, Pd, Os, Ir, Pt**

Noble metals are gold, silver, platinum group metals and their alloys. (Table 1.5). Electrical engineering and electro-technical industry consumes about 40 % of their production. There are microelectronic components labeled as „without noble metals” but yet still usually utilize golden micro-wires although the golden solder and gold coating have been largely replaced with other materials.

Gold has the highest corrosion resistance in atmospheric conditions. It does not react with oxygen. Therefore is used as protective coating on other metals in electronics. Gold is immune even in melted state, wets other metals which makes it perfect soldering material. It also wets silicon. It is difficult to replace gold solder in demanding applications. Its lower melting temperature is sometimes problematic during production of contacts – this sometimes leads to sticking of the contacts during its operation. Platinum is therefore more suitable in some applications, however its ability to catalyze organic compounds resulting in non-conductive layer on its surface restricts its use in other applications. Noble metals are characteristic for their stability in air and chemical resistance. Each noble metal has its unique properties, utilized in electro-technical components.

Silver and its alloys are widely used in electrical engineering industry. It is being used for its high thermal and electrical conductivity and the problems with surface forming sulfides have been overcome. The palladium is, thanks for its relatively low price, used more frequently. Noble-metals coatings on joints often react with the base metal forming intermetallic compounds with disadvantageous properties. Some noble metals are, in form of powders, used as conducting powders production for thick-layer applications.



**Table 1.5** Chosen physical properties of noble metals

| Properties                                      | Au                    | Ag                    | Pt                    | Pd                    | Rh                   | Ru                   | Ir                   | Os                   |
|---|-----------------------|-----------------------|-----------------------|-----------------------|----------------------|----------------------|----------------------|----------------------|
| Density [kg·m <sup>-3</sup> ]                   | 19300                 | 10500                 | 21450                 | 12000                 | 12400                | 12200                | 22400                | 22500                |
| $\lambda$ [W·m <sup>-1</sup> ·K <sup>-1</sup> ] | 312                   | 419                   | 74                    | 75                    | 88                   | 105                  | 59                   | -                    |
| $\alpha$ [K <sup>-1</sup> ]                     | 15,3·10 <sup>-6</sup> | 20,5·10 <sup>-6</sup> | 9,3·10 <sup>-6</sup>  | 11,5·10 <sup>-6</sup> | 9,1·10 <sup>-6</sup> | -                    | 7,1·10 <sup>-6</sup> | -                    |
| $\rho$ [μΩ·cm]                                  | 2,35                  | 1,59                  | 10,6                  | 10,8                  | 4,51                 | 7,6                  | 5,3                  | 9,5                  |
| $\alpha_R$ [K <sup>-1</sup> ]                   | 4,0·10 <sup>-3</sup>  | 4,1·10 <sup>-3</sup>  | 3,92·10 <sup>-3</sup> | 4,2·10 <sup>-3</sup>  | 4,4·10 <sup>-3</sup> | 4,1·10 <sup>-3</sup> | 43·10 <sup>-4</sup>  | 4,1·10 <sup>-3</sup> |
| $\gamma$ [%]                                    | 64,0                  | 108                   | 16,1                  | 17,4                  | 40                   | 23,6                 | 35,2                 | 18,4                 |
| $T_m$ [°C]                                      | 1064,4                | 961,9                 | 1769                  | 1555                  | 1963                 | 2334                 | 2447                 | 3003                 |

$\lambda$  - thermal conductivity coefficient at 20 °C,  $\alpha$  - thermal expansivity coefficient at 20 to 300 °C,  $\rho$  - resistivity at 20 °C,  $\alpha_R$  – thermal coefficient of electrical resistance at 0 to 100 °C,  $T_m$  – melting point,  $\gamma$  – specific conductance at 20 °C. Specific conductance  $\gamma$  is related to the conductivity of copper (in percent), for which the IACS (International Annealed Cooper Standard) set the value of 58 MS·m<sup>-1</sup>.

## 1.2 MATERIALS FOR CONTACTS

The term „contact” is used for the electrical contact between two conductors which can be switched on and off. There is a variety of connections which are switched during replacement of the component or its repair (soldered joint, rivet joint, welded joints), occasionally switched connections (wall sockets, plugs, connectors), and circuits which are switched relatively frequently (relay, change-over switches, controllers).

### Materials for electrical contacts are used in:

- 1) Power circuits for switching.
- 2) Current conduction for required time.
- 3) Interruption of power circuits.

### 1.2.1 Requirements

Materials for electrical contacts are required to have specific electrical, mechanical and thermal properties. No electrical contact can transport electricity without dissipation. Unwanted phenomena, such as warming of the material, transport of the material and oxidation, often occur in contacts during current transport. From the material point of view, the highest demands come from switching the power circuits during operation. Material requirements in this case are toughness and spring toughness. Bimetals are produced in form of strips, wires and profiles. Phenomena occurring during the contact operation need to be taken into account when choice the correct material:

1. **Low and stable contact resistance** – contact resistance needs to be small and stable during the whole lifetime of the component. These requirements are mostly met by the noble metals and their alloys. Materials need to be resistant in air, vapors, and oil; low oxidation ⇒ noble metals, carbon.
2. **Good electrical and thermal conductivity** ⇒ **Cu, Ag**  
 $\text{Ag} \sim \downarrow R_m, \downarrow HB \Rightarrow \text{Ag} + \text{Cu}$  are more viable  
 $\text{Ag} + 3.5\text{Cu} \sim \uparrow$  service life,  $\uparrow HB, \uparrow I, \uparrow U$   
Application: medium switching throughput, cam switches, mechanically stressed contacts.  
Powder metallurgy is preferred over melting and casting ~  $\downarrow$  decrease in el. conductivity.  
Material types: **AgNi, WCu, WAg (Cu, Ag ~ 20÷40 %)** so called **pseudo-alloys**.  
Production of pseudo-alloys: diffusion, capillary forces, infiltration (saturation by liquid metal).  
**Sintered carbides WC + 6 % Co** ~  $\uparrow$  hardness,  $\uparrow$  abrasion resistance (contacts for telephone relays (enhanced by addition of 1 ÷ 2 % Os)).
3. **Low burn-off, arcing resistance.** Higher throughput contacts are commonly spark eroded. The cause for this is melting, transport of the metal by sputtering or evaporation which takes place at high loads when an arc occurs. Their lifetime is predominantly determined by arcing (during the circuit switching off) which needs to be prevented. This can be resolved by proper material choice, or the circuit design, e.g. use of arc extinguishing circuit breakers (addition of capacitor with resistor, diode or resistor parallel to contact or inductance). The

design is based on limit conditions for arc occurrence which are determined by current and voltage on the contacts. Conditions need to be held below these parameters to prevent the arc to occur. Low burn-off of the contacts is crucial during higher contact load. Reduction in loss is the measured factor determining the life-span of the contact. Even if the arc does not occur, the voltage must be low enough to prevent ionization of the contact, and the current must be low enough to guarantee immediate interruption of the current flow.

Materials: W, C, W+Re (fine surface finish, slightly higher specific burn-off).

4. **Low creep**, otherwise the tips form on the surface, decreasing the contact area. Contacts cannot sputter and melt during the arc. The sputtering and melting results in transport of the material from one electrode to the other. This subsequently increases surface roughness of the contacts and proper connection cannot be achieved. As soon as the melting voltage of metals is reached, the migration of metals occurs. During voltage loading, certain point is reached, when the resistance is high enough to melt the material. Disconnection of the contacts results in erosion and transport of the metal to other place. Tips, typically forming on silver, are especially dangerous.

Materials: W, Mo, Au + 5 % Ni, Ag + CdO.

5. **Unwanted joining of contacts** – arc or even the passing current in closed circuit generates heat which makes the metal soft and also melts it. During cooling, the two metals can in fact form and weld joint. The materials with higher resistivity and hardness as well as low melting points are more prone to this. The material with low specific resistivity, low strength and high melting point should be used to avoid this kind of damage. Also, large contact area or multiple contact points are in this case desirable. “Joining” of the contacts occurs during normal loading even without current passing through the circuit, while the “welding” occurs only when melting voltage is reached. Joining is typical for noble metals with high diffusion coefficients (especially gold). It can be avoided by non-ferrous metals alloying, e.g. AuNi0.14 alloy. Welding tendency decreases using alloys with higher melting points.

Materials: Ag + Cu, C, CdO and others.

6. **Abrasive resistance** – materials with increased hardness. Abrasion is desirable to some extent as it practically removes the corrosion layers from the surface. This is further promoted by construction design. However, the abrasion lowers the life-span of the contact. Abrasion in rotary and frictional contacts (connectors, potentiometers) changes its electrical characteristic. Materials with dissimilar hardness are desirable in this application. Different materials or same materials with different thermal treatments are employed in this case.

Materials: Ag, Au, Cu + addition of elements: Ni, Si, Be.

7. **Chemical corrosion** manifests mainly by formation of oxide, sulfidic and other compounds on the contact, changing its properties. From the group of noble metals, silver is especially endangered by this phenomenon, because the silver sulfide forms even at room temperature. Unique problem is occurrence of brownish, porous layer on platinum contacts (*brown powder*) caused by catalytic activity of these metals on organic compounds resulting in solid sediments forming on its surface. This can be prevented by correct material selection.

Oxide application – increase in hardness, affects arc resistance (CdO has the greatest effect by lowering the arc energy).

Arc extinguishing – oxides with decomposition temperature (evaporation temperature) lower than silver (CdO, CuO, ZnO, SnO<sub>2</sub>, PbO, NiO).

Promoting of the arc formation – oxides with higher decomposition temperature than evaporation temperature of Ag (Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, MgO)

### **Classification of contacts and chosen materials:**

|                             |   |
|-----------------------------|---|
| Low throughput contacts     | - Ag, Au, Rh, Pd,                             |
| Creep-resistant contacts    | - Ag, Au, Pd, Pt,                             |
| Middle throughput contacts  | - Cu, Ag, W, AgNi, Ag-CdO, Ag-CuO and others. |
| Burn-off resistant contacts | - Mo, W, pseudo-alloys Ag-W, Cu-W and others. |
| Sliding contacts            | - Ag, Ag-C and others.                        |

## **1.2.2 Materials used for contacts**

### **A. PURE METALS**

**Pure silver** – silver is the most frequently employed material for contacts due to its excellent electrical and thermal conductivity and high resistance against oxidation.

Its main disadvantages are:

- formation of sulfide layer on the surface in atmosphere polluted with sulfur compounds,
- low abrasive resistance,
- low recrystallization and low melting temperature,
- arcing at low voltage and currents,
- relatively small mechanical strength,
- contacts weld at higher than 20 A throughputs.

Low melting temperature is problematic due to contacts joining (sticking together) and migration of the metal caused direct current. These disadvantages can be negated by alloying. Silver is used in form of massive rivets, plated contacts, bimetal contacts on different platforms and galvanic local or area-wide coatings. *Silver* is mostly used for plated contacts, in low throughput devices and silvering of low-cost contacts to enhance their surface properties.

**Pure gold** is the most noble metal with excellent electrical and thermal conductivity. Gold is immune to corrosion. It is stable even in polluted atmosphere and unlike platinum group metals does not catalyze organic compounds. These properties are also typical for gold alloys which can overcome the disadvantages of pure gold, such as: low abrasive resistance, low melting point and also tendency to material migration and contact welding. It is suitable for low throughput contacts with low friction forces, high switching rate and the allowable throughput is several milliamperes.

**Copper** is commonly used for low-cost contacts with high switching rate (non-conductive oxide forming on the surface is removed by the switching of the circuit). Commercially it is available in semi-hard or hard form.

**Platinum group metal materials** – contact parts are fabricated from platinum, palladium and iridium. All metals from platinum group have one major disadvantage – formation of polymer layer on the contact surface. This is most notable on Pd, followed by platinum.

**Platinum** has high chemical resistance, does not form oxide layer. Apart from good mechanical properties it is also abrasive resistant. Low burn-off rate is ensured by its high melting point. Disadvantages are lower electrical and thermal conductivity and high cost.

**Palladium** has very similar properties to platinum, but it is much cheaper. Disadvantage is its low oxidation resistance between 400 ÷ 800 °C. Typical application involves relay electronics in the form of rivet and desk contacts.

**Mercury** is suitable for contacts with low switching rate due to its very low contact resistance. Mercury contacts are nowadays being replaced by solid state power switches (human health issues).

**Tungsten** and **molybdenum** have high melting points and hardness also as resistance against the arc damage. It is suitable for high-throughput, abrasion, burn-off and welding resistant contacts. Used for high-voltage switches, relay switches etc.

**Graphite** – non-metallic material suitable for moving contacts in radial-operation devices and electric motors. Graphite brushes provide contact between immobile (stator) and moving part (rotor) of the machine. The brushes are fabricated from hard graphite, natural graphite, electro-graphite and metal-graphite. Brushes from hard graphite have relatively high resistivity toughness and hardness. Natural graphite brushes are soft, have good electrical conductivity and can withstand high centrifugal forces. Electro-graphite brushes have good toughness. They have a good electrical conductivity, resist to high radial velocities and high current throughput. Typically employed in large DC mining and rolling machines, commutator machines etc. Metal-graphite brushes have relatively low resistivity and are used in machines with lower operating voltage and high current levels. Brushes with higher copper content can be operated at higher currents, but lower radial velocities. Major advantage of graphite contact is that they don't suffer from burn-off and do not weld – carbon does not melt in arc. Although some of the carbon oxidation takes place **producing gaseous CO<sub>2</sub>** during arc extinguishing, the **newly-formed graphite surface remains clean**.

## **B. ALLOY MATERIALS**

### **B1. Silver alloys**

**Ag Ni0.1** – nickel has very low solubility in silver. Addition of 0.14 % Ni deteriorates its electrical and thermal conducting properties only slightly, while refining the structure, providing higher hardness and both low and high-temperature strength. Alloy is called ***fine-grained silver***. Alloys with higher nickel content (10, 15 to 40 % Ni) are produced by powder metallurgy and the higher nickel content lowers the erosion damage by arcing, enhancing abrasive resistance and hinders metal migration. However, electrical and thermal properties are worse. Application: contact material for medium-throughput switches.

**Ag-Cu** – alloying with small amounts of copper deteriorates the properties of silver only slightly, however the thermal and electrical conductivity decreases. Hardness, strength, burn-off and abrasive resistance are all increased, metal migration is lowered. Increased copper content lowers the chemical resistance. These alloys are applicable for switching currents up to 30 A and 220 V voltages. 3 % Cu is typically added. This alloy is called *hard silver*.

**Ag-Cd** – cadmium addition substantially worsens the electrical and thermal properties, but the burn-off resistance, abrasive resistance, welding and arc extinguishing properties are all strongly enhanced.

**Ag-CdO** – this alloy has higher conductivity than Ag-Cd and lower contact resistance even at lower pressures. Alloys with up to 15 % CdO are produced. Thin layer of CdO is formed on the contact surface after long-term annealing – with higher hardness than the original Ag-Cd alloy. It is produced from either mixture of Ag and CdO or Ag and Cd powders – CdO forms during switching electrical circuits. Decomposition of CdO at higher temperatures lowers the contact resistance. Ionization of cadmium vapors in electrical arc increases the diameter of the arc, the surface temperature is lowered and the arc is extinguished. All these combined hinders the welding of the contact surfaces. It has lower conductivity compared to silver. For its *arc-extinguishing* properties, the Ag-CdO alloy is used as main contact material up to 630 A throughputs and as contact material for circuit breakers up to 25 A throughputs.

**Ag-Pd** – palladium addition reduces the reactivity with sulfur and also enhances mechanical properties. It also increases the melting point of the alloy, the welding and joining is hindered, but most importantly, formation of sulfide layers is inhibited. It has low contact resistance. Only drawback is migration of material during DC switching. Alloys with palladium content of 3, 30 and 40 % are commonly available. Alloys with higher content of palladium tend to form brown powder on the surface. The material can be used in range of 2 A and 60 V.

**Ag-C** – non-metallic element graphite is added in range of 3 to 10 %. Composites with 3 % of graphite are most common. Alloy is highly resistant to oxidation. Contacts fabricated from this material are characteristic for their high el. conductivity, reliability and excel at welding resistance. The Ag-C contacts are usually used in combination with Ag contacts. This pair does not form weld even during very high current throughputs. This is utilized in railway transport for safety switches which must withstand short circuiting of large-capacity batteries. Drawbacks: carbon significantly decreases arc erosion resistance, alloys are difficult to work (by grinding) and weld.

**Ag-Cr<sub>2</sub>O<sub>3</sub>**. This material has about 1 % of chromium oxide and has the high resistance against contact welding.

**Ag-W pseudo-alloys** are produced by sintering of powders or heating of tungsten skelet with melt silver. They are utilized in special applications, where the low electrical and thermal conductivity of tungsten does not pose a problem (in more detail in section B5).

## **B2. Gold-base alloys**

**Au-Ni5** is the most important contact material alloys of gold. Good mechanical properties, low contact resistance and very low migration. Addition of nickel enhances mechanical properties of the alloy. 5 % of nickel basically prevents migration of the material while maintaining low contact resistance and corrosion resistance. Usable for throughputs of 5 to 100 mA with limit of 1 A at 12 to 60 V and can be also utilized in high-frequency circuits.

**Au-Ag-Ni3 alloys** were developed in effort to lower gold content. They have high hardness which gives them good abrasive resistance. Expensive alloy Au-Ni5 can be replaced by Au71-Ag26-Ni3.

**Alloy Au-Co5** has, compared to the Au-Ni5 alloys, higher hardness. Galvanic deposition can be employed to produce contacts.

## **B3. Copper based alloys**

**Metals and alloys for the base parts of contacts** are used for fabrication of contact lamellas, produced from infinite-length strips by cutting. Hard or flexible material is chosen according to the purpose of the contact. Nowadays, alloys are produced in strips of various thicknesses which make the design choices easier. **Copper** is used when a hard material with excellent electrical and thermal conductivity is required. Its strength at room temperatures is sufficient. The material requirements are very specific depending on the type and character of the contact. Easy and firm adhesion of the contact material is usually required – it is prepared by welding, soldering or riveting. The only drawback is that the flexible material loses its mechanical properties in the contact area during the thermal operations.

For **flexible lamellas**, **ECu, Cu-Fe2, Cu-Sn6, Cu-Sn8, Cu-Zn28, Cu-Be1,7, Cu-Be2, Cu-Ni18-Zn20** can be used according purpose. **Bronzes (beryllium, phosphorous)** are used in production of **flexible alloys**, **contact bimetals** or **thermal bimetals**.

**Contact bimetals** – goal is reduction in price by lowering the content of noble metals. These are produced by rolling of the contact material (Ag, Au, Pt and alloys) on the base part from the common metal or alloy (Cu, brass, bronze, steel etc.).

**Cu-Cr0.8** and **Cu-Ag4-Cd1** alloys exhibit better mechanical properties and oxidation resistance than Cu.

**Cu-C** is highly resistant against welding. It can also be used for friction contacts.

#### **B4. Platinum group alloys**

**Pt-Ir** is the most expensive contact material. It is employed whenever very low contact resistance and high burn-off resistance is required. They exhibit excellent resistance even in severely polluted atmospheres. Iridium addition hardens the alloy. Migration of metal at low current throughputs (fewer than 100 mA) causes formation of sharp edged deposits on the surface. At higher throughputs (tens of amperes) and voltage of 250 V, the abrasion damage is reduced, compared to gold or palladium alloys. Typical content of iridium is in range of 10 to 25 %. Apart from good mechanical properties, they also display high corrosion resistance; disadvantage is the low conductivity.

**Pd-Ag** outperforms other silver alloys. Alloys with up to 30 % Pd have significant corrosion resistance in sulfur-polluted atmospheres and high silver content hinders the catalytic effects of palladium.

**Pd-Cu** has higher burn-off and migration resistance compared to the Pd-Ag alloys. Usually contain 15 to 40 % Cu.

#### **B5. Pseudo-alloys – sintered materials**

Sintered materials have sufficient contact hardness, arcing resistance, good electrical and thermal conductivity. Heterogeneous systems of two or more metals, prepared by sintering mixture of powders or alloys prepared by reaction between porous base material and liquid of other metal(s) meet these requirements. **Tungsten** or **molybdenum**, in form of sintered skeleton filled with copper or silver, is typically used as base metals. The skeleton is highly abrasive and burn-off resistant, while the **Cu** or **Ag** provides good conductivity. Since the higher tungsten content decreases the conductivity, it must be adjusted according to the projected load. Contacts from these materials must be protected against air oxidation – for example by immersion in oil, because they form non-conductive oxide layer on its surface.

Production technology:

- Liquid copper and tungsten powder are mixed together and subsequently pressed and sintered at  $1300 \div 1400$  °C.
- Sintered skeletons from coarse-grained tungsten or molybdenum are filled with liquid copper or silver.

Sintered materials with W, Mo or Ni with various element ratios are produced under the name of ASKO.

**W-Cu** – labeled ASKO A40, ASKO A60, 67, 76 (value states the W content) are suitable for contacts in oil, throughputs up to 100 A, alternating 110 – 550 V voltage, with high mechanical stresses or shocks.

**W-Ag** - ASKO F30, 50 – used for high-switching performance contacts operated in air. Good welding resistance. It is utilized as starter switches, tram control circuits, trolleybuses, and locomotives.

**Ni-Ag** – 40Ni-Ag, 60Ni-Ag alloys have, apart from good electrical and thermal conductivity, high burn-off and welding resistance and also lower contact resistance. It is suitable for lower voltage and high current circuit switching in aerial condition. Their lower hardness limits their application to circuits without mechanical shocks or high contact forces.

#### **B6. Rubber contacts**

Advantageous properties of silicon rubber are utilized in rubber contacts. Contact material is usually conductive silicon rubber and the flexible part of the contacts is the non-conductive rubber. The additives providing conductive properties deteriorate its elastic behavior – therefore combination of two types of rubber is utilized. By changing the shape of the contact spring, different contact forces curves are achieved which is used to provide perfect contact. Planar plates are widely used in rubber contacts. Rubber contacts are used in **calculator and PC keyboards**, watches, typewriters, Telex devices and remote controls.

#### **Production and construction of contacts**

**Types of contact profiles** (Fig. 1.5):

- Wire, tube and rod contacts. These are for example plugs, wall and tube sockets.
- Strip or sheet contacts – planar, bent and brush contacts.
- Sintered metals contacts in form of discs, plates, and plugs. They are fabricated by metal powder sinteration.
- Cast contacts. They are produced in all shapes by cutting.
- Rivet, screwed and welded contacts. In planar, lens or tip contacts.

**Shapes of rivet contacts:**

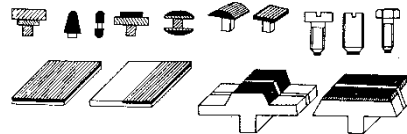
- contacts with lens head
- contacts with conic head
- contacts with round head
- contacts with planar head
- contacts with tapered head



**Fig. 1.5** Different shapes and types of contact

**Shapes of rivet contacts:**

- round contacts (diameter of 2,5 ÷ 6 mm)
- tetragonal (4,5 x 4,5 ÷ 10 x 10 mm)
- rounded (14 x 14 ÷ 25 x 25 mm)



**Examples of contact application**

**Circuit breakers** – if the melting and welding of the contact during current overload and short-circuiting are of an issue, combination of hard material and well conductive material (silver-plated) is chosen.

**High-performance switches** – for switching of high-voltage and high-current circuits and for circuits where arcing could occur, it is necessary to use a material with high melting point that does not weld (eg. tungsten with other good conducting material or sintered material).

**Friction contacts (control resistor)** are produced either from copper, bronze, or from noble metals for precise portable resistors.

**Friction contacts (tram trolleys, electromotor brushes, generators)** are commonly fabricated from mixture of Cu, Ag and graphite powders. Metal content varies depending on the current throughput from 50 to 95 %.

**Trolley skids** – made from mixture of Fe and graphite (less prone to mechanical shock damage when the skid slides over different direction wires on crossings). Their properties can be enhanced by silver.

**Strongly mechanically stressed contacts** – copper, alternatively sintered with W.

**Frontal contacts** – most frequently silver.

**Contact relays** – for frequent switching of low throughput circuits with low voltage usually made from rare metals and alloys with higher melting point, higher contact resistance is otherwise an issue which subsequently leads to joining and migration of material.

# 2. SPECIAL CONDUCTIVE MATERIALS

## 2.1 MATERIALS FOR RESISTORS

**Desired properties** for high-resistivity materials (also called resistance materials):

1. high specific resistivity,
2. low or zero temperature coefficient of electrical resistance  $\alpha_R$ ,
3. long term stable properties,
4. non-reactive with the environment at operation temperatures,
5. low thermoelectric voltage compared to copper,
6. good malleability for easy forming of semi-finished or final product.

Resistivity of resistance material is usually in range of  $0.2 \mu\Omega\cdot\text{m}$  to  $2 \mu\Omega\cdot\text{m}$  which is 10 to 100 times more than materials with high conductivity. Temperature coefficient of electrical resistance is usually around  $10^{-6}$  to  $10^{-4} \text{K}^{-1}$ . High-resistivity materials are usually alloys. These materials are used for production of resistors, whether for transformation of electrical energy to heat (resistor heaters) or measurement resistors and control devices or other applications in electronics and electrical engineering. Materials for resistor heaters are required to have high strength at elevated temperatures, high oxidation resistance, high thermal stability and heat resistance. Resistors for measuring devices ought to be made of materials with low (or zero) thermal coefficient of electrical resistance. Properties of chosen resistance materials for measuring devices are listed in Table 2.1.

### 2.1.1 Resistance materials for measuring devices

Materials from this group (Table 2.1) are used for production of resistance wires used for:

**a) precise measurement purposes**

Materials for wire resistors with  $\pm 0,001 \%$  precision, e.g. resistance standards or resistance sets. They are required to have high specific resistivity, low thermal coefficient of el. resistance  $\alpha_R$ , low thermoelectric voltage and high stability. Applicable usually at the temperature about  $20 \text{ }^\circ\text{C}$ . Examples of materials of this group: manganin, isotan, zeranin, isaohm, stabilohm, microthal, gold-chromium, or constantan.

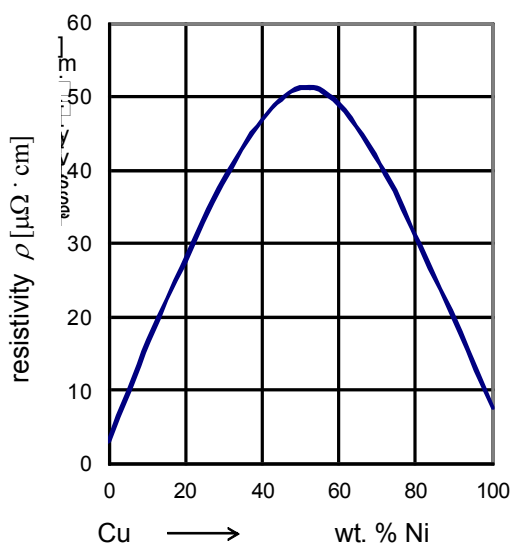
**b) control and switching purposes**

Materials for control, switching and series resistors are required to have to be, apart from the previously mentioned characteristics, highly stable in operation temperatures up to  $200 \text{ }^\circ\text{C}$ . Examples of materials of this group: constantan, nickelin; for some other applications also cast iron.

**Table 2.1** Chosen resistance materials and their properties

| Resistance material  | Chemical composition [wt. %]      | Resistivity $\rho$ [ $\mu\Omega\cdot\text{m}$ ] | Thermal coeff. of el. resistance $\alpha_R \cdot 10^6$ [ $\text{K}^{-1}$ ] | Ultimate tensile strength $R_m$ [MPa] | Relative thermoelectrical voltage (relative to Cu) [ $\mu\text{V}\cdot\text{K}^{-1}$ ] | Max. operation temperature [ $^\circ\text{C}$ ] |
|----------------------|-----------------------------------|---|--|---------------------------------------|--|---|
| <u>Manganin</u>      | 86 Cu 12 Mn 2 Ni                  | 0.43  | $\pm 2,5$ ( $20 \text{ }^\circ\text{C}$ )                                  | 500÷550                               | -0,6   | 140   |
| <u>Zeranin</u>       | 87 Cu 7 Mn                        | 0.43  | $\pm 3$ ( $20 \text{ }^\circ\text{C}$ )                                    | 350÷400                               | -1,3   | 140   |
| <u>Constantan</u>    | 54 Cu 45 Ni 1 Mn                  | 0.5   | $\pm 50$ ( $20 \text{ }^\circ\text{C}$ )                                   | 400÷500                               | -40  | 500   |
| <u>Isotan</u>        | 55 Cu 44 Ni 2 Mn                  | 0.49  | +40; -80   | 450÷550                               | -42  | 600   |
| <u>Nickelin</u>      | 67 Cu 30 Ni 3 Mn                  | 0.4   | $\pm 180$ ( $20 \text{ }^\circ\text{C}$ )                                  | 350÷400                               | -20  | 400   |
| <u>Nicrothal LX</u>  | 75 Ni 20 Cr 5 Si+Mn               | 1.33  | 10   | 1100÷1400                             | max. 1   | 300   |
| <u>Isaohm</u>        | 74 Ni 20 Cr 1 Mn                  | 1.32  | $\pm 10$ ( $20 \text{ }^\circ\text{C}$ )                                   | 1100÷1200                             | +1   | 250   |
| <u>Stabilohm</u>     | 80 Ni 20 Cr                       | 1.33  | $\pm 5$ ( $20 \text{ }^\circ\text{C}$ )                                    |                                       | +0,5   | 250   |
| <u>Au – Cr alloy</u> | 97.95 Au 2.05 Cr                  | 0.33  | $\pm 1$ ( $20 \text{ }^\circ\text{C}$ )                                    |                                       | 7  |   |
| <u>Chrom-nikl</u>    | 80 Ni 20 Cr                       | 1.1   | 85   | 700÷1400                              | 5  | 1200  |
| <u>Cekas</u>         | 60÷65 Ni 15÷19 Cr 15÷20 Fe 2÷4 Mn | 1÷1.13  | 70   |                                       |  | 1050  |
| <u>Canthal A</u>     | 70 Fe 23 Cr 4.5 Al 1 Co           | 1.39  | 49   | 650÷850                               |  | 1300  |
| <u>Canthal Al</u>    | 68 Fe 24 Cr 5.5 Al 1.5 Co         | 1.45  | 32   | 650÷850                               |  | 1350  |
| <u>Canthal DS</u>    | 72 Fe 22 Cr 4 Al 0,7 Co           | 1.35  | 63   | 650÷850                               |  | 1150  |
| <u>Čechral</u>       | 81 Fe 14.5 Cr 4.5 Al              | 1,3   | 180  |                                       |  | 850   |

- Manganin** is a **manganese bronze** with reddish color. Contains copper, 12 % Mn and 2 % Ni. Material for fabrication of **precise and stable resistors** with  $\pm 0.1$  to  $\pm 0.001$  % precision limits. Commercially available in the form of wire with diameter of up to 0.05 mm, strips or foils. The thermal dependence of resistivity is parabolic. Due to the instability of their properties, the manganin resistors are aged after their fabrication. Resistors insulated by coil wiring are thermally aged in several cycles. First stage of each cycle is aging at 120 °C, followed by resting at room temperature. Resistors with non-insulated coil wiring are firstly electrolytically coated with silver and then aged at 400 °C. Silver, preventing manganese from evaporating at higher temperatures, is etched afterwards. Planar resistors are the second type of manganin resistors. These are fabricated by gluing manganese foils (0.01 mm thickness) on both sides of laminated paper and etched in the shape of meander. Manganin is also used for **resistive pressure gauges** which change their resistance with pressure.
- Zeranin** is resistive material containing copper and manganese with addition of germanium. Its properties are very similar to those of manganin. Used for fabrication of precise resistors.
- Constantan** is a **nickel bronze** (45 % Ni) with addition of 1 % Mn (Fig. 2.1). Cu-Ni alloys exhibit perfect mutual solubility in both liquid and solid state (identical crystal lattice, similar atom size and similar bond character). Alloys with higher Ni content are ferromagnetic. They also have good strength at normal and elevated temperature, sufficient stress corrosion cracking resistance and also have **high electrical resistance which is only little temperature dependent!** Used as **coil wiring** of common **resistors** with  $\pm 0.5$  % accuracy, for production of **thermally stable resistors** and for **thermoelectric couples** applicable at temperatures up to 600 °C. Thinnest wires are suitable for **resistance sensors of strain gauges** for mechanical strain measurements.



Constantan has not only high specific electrical resistance, but also low thermal coefficient of electrical resistance. High thermoelectric voltage relatively to copper however prevents from using constantan for precise resistor for DC circuits. The thermal coefficient of electrical resistance  $\alpha_R$ , which is usually negative and thermal-independent, can be adjusted by changing the manganese content (typically up to 1 %). The resistance of copper wires during temperature changes can be compensated with constantan. Nickel addition is sufficient to provide good resistance against ammonia vapors.

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**Fig. 2.1** Influence of chemical composition of Cu – Ni alloy on resistivity

**Cu-Ni-Al** (Cu Ni6 Al1) – high oxidation and high-temperature resistance. Cast and formed alloys: complex alloys with low amounts of Ni, Si, Be, Al, Cr, Co, V, Fe (application: weld electrodes, thermally stressed aircraft components etc.).

- Nickelin** is a **nickel bronze** (30 % Ni) with 3 % of **manganese**. Used for fabrication of resistor which are not required to have stable resistance – regulation and switching purposes (technical rheostats, regulation resistors). Oxide layer can be prepared by annealing in oxidation atmosphere. This layer has sufficient resistance to facilitate an insulator for common use.
- Isotan** is used for common resistors production.
- Isaohm, microthal, stabilohm** are resistive Cr-Ni alloys. They have relatively high specific resistivity of around 1.3  $\mu\Omega \cdot \text{m}$ . Used for precise resistors with high resistance wiring.
- Au-Cr alloy** – gold content is higher than chromium content. Maintaining the content of chromium at 2.05 % has significant effect, especially on thermal coefficient of electrical resistance  $\alpha_R$ . This material is used for production of precise resistors and resistance standards. Alternatives with lower cost are preferred. Au with 2 % Cr alloy annealed for several days in vacuum is completely stable at 150 °C. Its electrical resistance is temperature independent in wide temperature range. However, it is strongly affected by mechanical strain in the structure, for example occurring during humidity level changes. To assure precise measurement, these standards are set in argon filled casing.
- Cast iron** has specific resistivity of 0.7  $\mu\Omega \cdot \text{m}$  and highest allowable operation temperature of 500 °C. It is used for manufacture of planar segments for power switches.



9. **Cu–Ni–Zn alloy** (54÷60 % Cu, 17÷26 % Ni, 20÷23 % Zn). Resistivity of  $0.3 \div 0.4 \mu\Omega\cdot\text{m}$  (at 20 °C), ↓ stability (Zn addition) → max. operation temperature 350 °C.
10. **Nimonic 80A** (73.1 % Ni; 19.4 % Cr; 2.5 % Ti; 1.3 % Al; 1.1 % Co; 0.74 % Si; 0.6 % Fe; 0.25 % Mn; 0.1 % C) – withstands high loads, 3 times higher resistivity than manganin, suitable to use in temperatures up to 100 °C.
11. **Ag alloys** e.g. 91 % Ag + 9 % Mn for precise resistors, 78÷85 % Ag + 8÷17 % Mn + 3÷9 % Sn for common resistors. Very low thermal coefficient of electrical resistance  $\alpha_R$ .
12. **Mn–Ni–Cu alloys** have the highest thermal coefficient of el. resistance of all mentioned alloys, roughly 5 times greater than manganin. Apart from that, also exhibit low thermo-electrical voltage, are malleable. Can be drawn into very thin wires.
13. **Ni–Cr–Al alloys** have 3 times the specific resistance of manganin and lower thermal coefficient of electrical resistance. Their resistance is less temperature dependent in the –55 to +100 °C range than manganin. The thermal coefficient can be further lowered by suitable thermal treatment to  $-0.0005 \text{ K}^{-1}$ . Their resistance doesn't change during operation exposure. These alloys can be drawn to very thin wires (10÷15  $\mu\text{m}$  diameter). These alloys enabled miniaturization of resistors. Another advantage is their resistance against surface oxidation at elevated temperature. Soldering is complicated due to formation of chromium oxides, however these can be removed by correct soldering technology.

## 2.1.2 Resistance materials for heating devices

Materials from this group are employed as heating segments of heating devices (irons, cookers) and electrical furnaces. Allowed operation temperatures are between 500 to 1350 °C. At these temperatures, material chemically reacts on the surface with atmosphere and even with other adjacent materials. Oxygen, nitrogen, sulfur, carbon but also ceramics cause the heating segment material deterioration which can eventually lead to its failure. Resistance materials for heating devices are required to have high specific el. resistance and low thermal coefficient of el. resistance but also the coefficient of thermal expansion needs to be low to prevent the heating segment from becoming loose. High heat resistance, i.e. oxidation resistance and operation lifetime are of special importance. Cr–Ni, Cr–Ni–Fe and Fe–Cr–Al alloys preferred for the heating segments production.

1. **Cr–Ni alloy** contains 20 % of chromium and 80 % of nickel. It is called **chromnickel**. Specific resistivity at 20 °C is  $1.09 \mu\Omega\cdot\text{m}$ ,  $1.16 \mu\Omega\cdot\text{m}$  at 1000 °C. Commercially available in form of wires with diameter of up to 0.01 mm and strips. It has very high thermal resistance – operation temperatures can go as high as 800 to 1200 °C. Chromium oxide forming on the surface enhances the chemical and oxidation resistance as well as mechanical shock resistance of the material. However high nickel content increases its price. Chromnickel is employed as coil wiring of common resistors for electrical ovens and cookers. Compound thin-plate resistors are produced by deposition of the alloy on ceramic (fosterite) plate.
2. **Cr–Ni–Fe** is based on chromium and nickel. Chromium content is about 20 % in all alloys of this group, nickel content varies from 20 to 80 %. Nickel increases its specific resistivity – from 0.95 to  $1.1 \mu\Omega\cdot\text{m}$  as well as the heat resistance of the alloys; their allowed operation temperature rises from 900 to 1200 °C. Alloys of this group are labeled CN 20, CN 30, CN 60 and CN 80 (number indicates % of nickel content). Commercial names are **cekas**, **feronichrom**, **ferochronin**. Cr–Ni–Fe are cheaper than Cr–Ni alloys, but with worse properties. Increasing the iron content lowers the operation temperature and their oxidation resistance.
3. **Fe–Cr–Al alloys** usually contain 20 to 30 % of chromium, 3 to 6 % of aluminum and iron balance. Their structure is ferritic; they are harder, more brittle and have lower formability compared to the Cr–Ni–Fe alloys. Their specific resistivity is high:  $1.25$  to  $1.45 \mu\Omega\cdot\text{m}$ . Aluminum addition forms protective layer of aluminum oxide on its surface which increases its allowable operation temperature up to 1350 °C. 2÷3 % of silicon has similar effect. Domestic available Fe–Cr–Al alloys are labeled AC 20, AC 22, AC 30, where the number states the chromium content in %, Fe–Cr–Si alloys with silicon are labeled SC 20 and so forth. Alloy “**Canthal**”, contains, besides **iron**, **chromium** and **aluminum**, also 0.25 to 3 % of **cobalt**. It is being produced in various categories, e.g. Canthal Al for use at up to 1350 °C, Canthal A (up to 1300 °C) and Canthal DS (up to 1150 °C). These alloys are sometimes also called **fechral** and **chromal**. Temperature limit for Fe–Cr–Al is 1350 °C; they become brittle and soft at higher temperature which significantly reduces its lifetime.

## Resistance materials for elevated temperatures

Non-metallic materials are usually used for applications at temperatures above 1350 °C, however certain metallic materials with high melting points can also be used. Metals, with the exception of platinum, begin to oxidize long before reaching their melting points. For high-temperature application, these metals need to be placed in vacuum or in protective atmosphere (inert gasses or others). Tungsten filament in vacuum tubes or light bulbs is typical example.

Temperatures above 1350 °C – **noble metals** (Pt, ...)

Temperatures up to ~ 1700 °C - **W, Mo** (reduction/inert atmosphere or vacuum is necessary).

### 2.1.3 Non-metallic resistance materials

Materials from this group can be used at temperature over 1350 °C, when metallic resistance materials lose their mechanical properties and their lifetime is significantly reduced. Non-metallic silicate or carbon materials have, compared to the metallic materials, much higher specific resistivity.

1. **Silite** is a mixture of **silicon carbide or carbide** with other elements. It is used to fabricate heating elements in form of rods and tubes, by pressing and sintering the mixture. **Silite resistors** (Si + C + SiC) in the form of rods and tubes, temperature ~ 1450 °C, resistivity ~ 0.1 to 0.2 Ω·m, brittle material up to 900 °C ~ negative  $\alpha_R$ . Electrical resistance over 1000 °C changes only slightly,  $\alpha$  is positive. These materials can be used up to 1600 °C. Silite products are distributed under brand name **globalar, quarzilit, crusilite** and others.
2. **Carbon heating segments** are fabricated by pressing the mixture of carbon black (soot) as the conductive part of the mixture and phenol-formaldehyde resin (non-conductive) in rod, tube and plate shapes. Applicable up to 2500 °C.
3. **Heating elements for temperatures up to 2600 °C** are produced by sintering **tungsten** or **molybdenum powder** (conductive compound) with **aluminum or zirconium oxides** (non-conductive compound) which have melting point higher than 2000 °C.
4. **Supercanthal Mo-Si** (based on  $\text{MoSi}_2$  compound) for temperatures up to ~ 1600 °C. Suitable for oxidation atmospheres.

### Technical carbon, graphite, electro-graphite

Fabrication of electro-graphite is similar to fabrication of ceramics. The natural graphite is milled with coal, coke, anthracite and electro-graphite machining waste. Those are mixed with hard coal, thus forming malleable mass. Different kinds of graphite require different raw materials. The semi-finished products are pressed to blocks or by an extrusion press. Pressing technology affects the graphite structure and its resistivity. Pressings are then annealed for about 4 weeks at 1200 °C forming hard carbon (basically a bonding agent) and coke. Its use in electrical engineering is very limited due to its poor workability. This is improved by electro-graphite process. Components are heated by DC source to 2500 °C, changing the coke to electro-graphite followed by crystallization. Most of the impurities evaporate, however higher purity can be achieved by filling the reaction chamber by gaseous hydrogen chloride during the final annealing step, keeping it in place until the product cools down.

Semi-finished products from pure graphite are in form of plates, blocks, rods and tubes. Machinability of graphite is limited, since it reacts with oils and oil vapors. It can be cut, lathed, drilled, shaped and also ground and polished. Graphite is brittle. Annealing the graphite at 150 °C for one minute is sufficient to dry it completely. However, most of the semi-finished products are subsequently annealed in vacuum.

Semi-finished products for use in vacuum or protective atmosphere must be degassed by vacuum annealing. This is facilitated by annealing at 1700 to 2500 °C at  $1 \cdot 10^{-2}$  Pa or lower pressure. This removes the nitrogen, sulfur and alkalis. Desorption rate is very low; placing the product in PE (polyethylene) bags is sufficient.

Graphite has hexagonal lattice structure; individual layers of carbon atoms can shift respectively to each other which explains their abrasion and excellent lubrication properties; this is not completely true in vacuum.

**Application of graphite:** Electrical engineering industry has a broad spectrum of application for graphite for its numerous advantageous properties; mostly in form of synthetic graphite (electro-graphite). These properties are utilized:

- **High temperature resistance:** Sublimation temperature is roughly 3400 °C; the carbon vapor pressure at this temperature is around  $1.33 \cdot 10^{-6}$  Pa. Similarly to tungsten and tantalum, its strength increases with temperature. If present, pyrolytic graphite layer on the surface gets burnt-off above 800 °C, otherwise the burn-off starts at temperatures as low as 550 °C. However this layer on graphite surface deteriorates its resistance to thermal shocks.

- **Resistivity:** is lower along the carbon layers ( $15 \mu\Omega\cdot\text{m}$ ), higher across the layers ( $24 \mu\Omega\cdot\text{m}$ ). Is not strongly affected by temperature and it reaches minimum between 400 to 800 °C. The resistivity at 2200 °C is practically identical as at room temperature.
- **Thermal expansivity:** thermal expansion coefficient is about  $3.5\cdot 10^{-6} \text{ K}^{-1}$  in the plane perpendicular to the grain lattice and about  $2\cdot 10^{-6} \text{ K}^{-1}$  in parallel plane. It is lower compared to metals, but higher than fused quartz glass. This is significant for joining graphite and metals or for application of graphite as lining for fused quartz cups, e.g. production of silicon by Czochralski method or production of semiconductor compounds of A<sup>III</sup>B<sup>V</sup> type. It is also used as mold material for fused quartz products.
- **Glass wetting:** Graphite doesn't wet glass which is convenient for fused quartz and glass-metal seals. Metals need to be oxidized in strictly neutral atmosphere before seal fabrication.
- **Chemical purity:** Pure electro-graphite contains less than 100 ppm of ash.
- **Chemical resistance:** Graphite is resistant to most of the common acids and alkalis, only reacts with certain substances with which it forms lamellar compounds. These are for example fluorine, boron, potassium, sulfur oxide, ferric chloride and oil. It also reacts with concentrated nitric acid. Most metals react with carbon at high temperatures forming carbides. Since carbon isn't wetted by liquid metals, it is often used as a material for **for noble metals melting cups, as well as for aluminum, germanium and some semiconductor compounds (A<sup>III</sup>B<sup>V</sup> type)**, and others.
- **Graphite behavior in neutral atmosphere:** Graphite contains about 50 ppm of hydrogen which, at high temperatures, diffuses towards the surface and reacts with carbon at specific conditions forming hydrocarbons. These escape from the surface and are then decomposed back to the hydrogen and graphite which deposits at cooler areas such as beakers and insulation parts of the component.

## 2.1.4 Electrical engineering components utilizing the resistance materials

**Resistors** are passive electronic components which are characterized by their resistance  $R$ . Another important parameter is specific dissipation factor. Dissipative factor is the throughput that is low enough so the produced dissipative heat doesn't cause the component to exceed the limit value. The temperature depends on the construction design of the resistor. Wire resistors have coil of resistance wire on a bearing wire or a tube. Wire ends are welded to the contacts which are similar to the contacts of the composite resistors. The surface of the wire resistors is commonly coated by a layer of special cement or enamel which provides protection up to several hundreds of °C. The surface temperature of some wire resistors during operation reaches 350 °C. Heat radiation is very efficient at these temperatures so their surface can be much smaller than size of planar resistors for the same purpose. All common resistors have significant inductance which limits their application to DC or low-frequency AC circuits. Some kinds of wire resistors are equipped with branching. Branching contact is facilitated by metal strip around its body, connected to the resistance coil wiring side without the protective layer of cement (shallow groove longitudinal to the resistor body). The branching contact location cannot be repeatedly altered.

**Planar resistors** are fabricated as thin layer on the cylindrical or plate support ceramic plate (usually corundum  $\text{Al}_2\text{O}_3$ ) or thick-layered on enameled metallic or ceramic support (corundum).

**Thin-layer resistors** have carbon or metallic functional layer (e.g. nichrom, canthal). Carbon layer is fabricated by pyrolysis (thermal decomposition of carbon). Metallic layers are deposited chemically, by cathodic sputtering or vapor deposition in vacuum. Specific resistivity is reached by grooving – part of the layer is removed (by laser, grinding, sanding).

**Thick-layer resistors** – functional layer consist of resistive paste (carbon, ruthenium, iridium, cadmium) deposited by screen and later burnt. The past also contains some organic compounds which provide desired viscosity and act as filler material used to achieve specific resistance, also providing good adhesion to the substrate. This organic compound is removed during the burning process.

**Variable resistors, resistance trimmer** are produced exclusively in rotary configuration. Trimmer is not designed to be rotated many times. The resistance track is made from the same material as the material for planar resistors – this layer is deposited on the base plate from laminated paper or ceramic. The contacts are adjusted to fit in printed circuit boards.

**Potentiometers** can be made with specific response (N, G, E...) of the resistance track. Configuration is either rotary or slider-like.

Rotary potentiometers are further divided into simple (singular system), simple with off-switch, dual (two systems in the same casing with independent control in the same axis), tandem (two systems in connected casings operated by the same control – concurrence accuracy is essential).

**Sliding potentiometers** – produced in simple, tandem or dual configuration. Divided according to the resistance track response:

linear – N, logarithmic – G, exponential – E, logarithmic with branching – Y.

Required properties of the potentiometers are: continuity of resistance track response, resistance stability, minimal noise during sliding, long service life, low cost.

Potentiometers can be, from the technological point of view, divided to:

### **Planar potentiometers**

The resistance track of typical common and cheapest potentiometers is made from special varnish with soot additive. Track is not very resilient, the service life of such potentiometer is low. Higher-quality potentiometer have the resistance track made of hard carbon or cermet. (Cermet is a mixture of ceramic and metal - special kind of glass with dispersed noble metal powder). These potentiometers have very stable resistance, long service life and low levels of noise.

### **Pull potentiometers**

This kind of potentiometer consists of resistance track and collector. Collector can be moved along the resistance track. The shape of the resistance track needs to be adjusted to the mechanism of collector movement.

### **Wire potentiometers**

For the electrical engineering, the wire rotary potentiometers are produced. Their resistance track is basically reeled on horseshoe shaped isolation plate. Fabricated products have linear resistance response. For precise and fine adjustable resistance potentiometers, the configuration which allows for 10÷20 turns, are also fabricated (in Czech Republic produced under brand name Aripot).

**Thermistors** with negative thermal coefficient of el. resistance  $\alpha_R$  (labeled NTC) which are resistors with el. resistance controlled by temperature. Other kind, labeled PTC has opposite temperature dependency (positive  $\alpha_R$ ). These are produced from metal oxides (semiconductor character), for example from ferric and titanium oxide mixture. Their properties are determined by the composition and fabrication method. The response stability is ensured by sealing it into casing with atmosphere.

**Application:** measuring, compensation and control components.

**Varistors** – voltage dependent resistors for low throughputs (labeled VDR). Their resistance changes with voltage without delay. This phenomenon is caused by the increase of free electron amount with voltage increase. Material for varistor production is polycrystalline silicon carbide with suitable filler. This material is then pressed into various shapes and sintered at 1000 to 1300 °C.

**Application:** overvoltage protection components, arcing-prevention, sparking prevention, voltage stabilization, multiplication of frequency and the time-response alteration.

## **2.2 MATERIALS FOR THERMOELECTRIC TRANSFORMATION**

### **2.2.1 Theory of thermo-electricity**

Thermoelectric effect can be defined as transformation of electrical energy to heat and vice versa. Devices to facilitate this transformation are called thermoelectric sources or thermoelectric couples.

#### **Contact voltage**

Contact between two dissimilar metals creates a difference in their contact potential. This difference is called contact voltage. Its magnitude depends on chemical composition of connected metals and their temperature. A. Volta divided metals into a series, where, if metal is connected with other metal further in the series generates positive voltage response: Al, Zn, Pb, Sn, Sb, Bi, Hg, Fe, Cu, Ag, Au, Pt, Pd. However this effect cannot be used for power generation, since the contact voltage in closed circuit is negated. This is valid only if the temperature of both contacts is identical.

#### **Seebeck effect**

Two conductors from dissimilar metals at different temperature  $T_1$  and  $T_2$ , connected to a closed circuit, generate electrical flow in the circuit – Fig. 2.2. This explains the Seebeck effect.

Thermoelectric voltage is insignificant for most metal couples and only 1 to 3 % of the induced heat can be transformed to electricity. This is why thermoelectric couples haven't been used as power sources in the past, but were frequently used for temperature measurements in laboratory conditions and in industry.

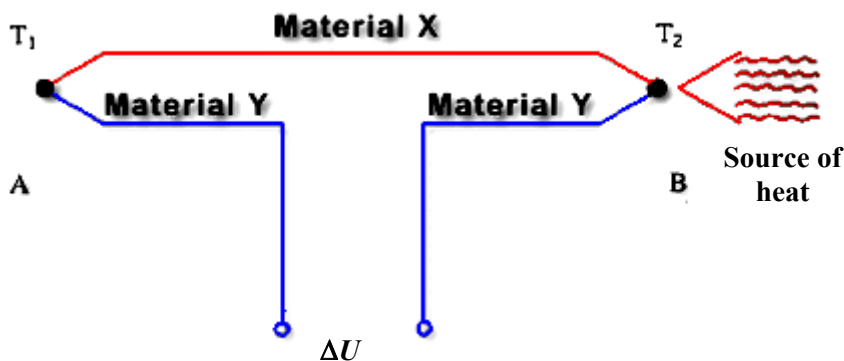
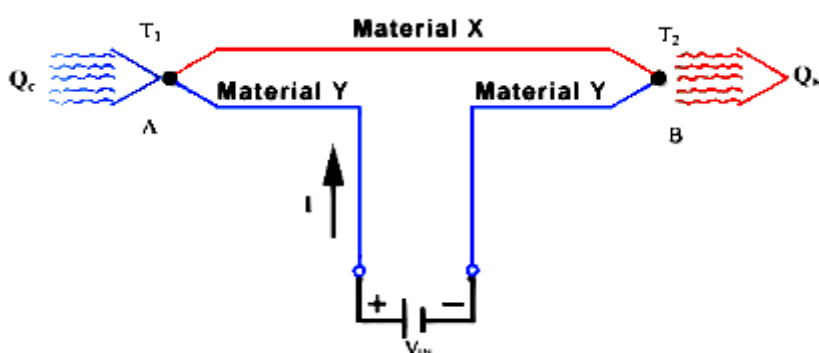


Fig. 2.2 shows that if the temperature difference  $\Delta T = T_2 - T_1$  between the contact points of the conductors is maintained, the voltage  $\Delta U$  can be measured. At small  $\Delta T$ , the measured  $\Delta U = \alpha \Delta T$ , where  $\alpha$  is the thermoelectric coefficient of the conductor. This coefficient is in  $10^{-6} \div 10^{-5} \text{ V}\cdot\text{K}^{-1}$  magnitude for metals,  $10^{-5} \div 10^{-3} \text{ V}\cdot\text{K}^{-1}$  for semi-conductors.

Fig. 2.2 Principle of Seebeck effect

### Peltier effect (Fig. 2.3)

If there is an electrical flow in the Seebeck circuit induced by external power source, thermal difference occurs between the two conductors. If the current, induced by external power source, flows in the same direction as the current flow caused by the Seebeck effect, then the metals connection consumes heat.



The connection generates heat if the current flow is reversed. Peltier effect depends on the metal composition and their temperature. It is the direct opposite of the Seebeck effect. Application of Peltier couple is very broad, for example air conditioning, cooler units for amplifiers, microprocessors, small AC units, cooling boxes for groceries, portable fridges and other.

Fig. 2.3 Principle of Peltier effect

### Thomson effect

Third thermoelectric effect was discovered and experimentally verified by W. Thomson using this experiment: if the long metallic rod is heated in the center, thermal gradient on both sides occurs. Both ends have the same temperature. Electrical flow induced to the rod during heating causes one part of the rod to become cooler and the other part to become hotter. Temperature distribution is not symmetrical.

**Thermocouple** is a circuit consisting of two dissimilar metal conductors with different electron work output for each metal. Consequently, contact potential is generated at the connection point which also increases with temperature. If both metals have the same temperature at the contact point, their potential is also the same, the sum is zero due to the opposite charge of the contacts. Only if the temperature on the contact points differs, the potential is not unite and voltage (on the thermocouple) is therefore generated. The voltage is called Seebeck thermoelectric voltage. Thermocouple can be therefore used as a power source.

Seebeck thermoelectric voltage  $U_e$  is proportional to the temperature difference of the thermocouple contacts. However, increase of the temperature difference between the two connected metals results only in several tens of microvolts change at the contact points.

Seebeck thermoelectric effect is utilized mostly in temperature measurements. Milivoltmeter is firstly connected to the opened circuit, measuring the thermoelectric voltage of the contact. The “cold” conductor is held at set temperature (usually submerged to water-ice mixture  $0^\circ\text{C}$ ), while the measurement (also called “hot”) conductor is placed on a spots where the temperature is to be measured.

Thermoelectric voltage  $U_e$  is linearly proportional to the temperature difference of the two contact points; this relationship is, at higher temperature, described by quadratic equation

$$U_e = a(T_2 - T_1) + b(T_2 - T_1)^2,$$

$a, b$  are coefficients characteristic for the chosen thermocouple type.

Certain requirements must be taken into account when choosing materials for the thermoelectric sensor. First of all, the voltage-temperature dependency must be approximately linear. Material needs to be chemically and

mechanically stable and also needs to have good corrosion resistance. The output voltage must be as high as possible. Low voltage values also reduce the accuracy of the device. Sensors from brittle metals (bismuth, antimony etc.) need to be joined (by spraying or sintering) in vacuum.

The temperature range and desired accuracy both need are also important when choosing the material for the thermocouple. Its stability or medium life-span is an important factor. The voltage response needs to be stable over the whole service life. This is especially problematic at higher temperatures. The contact material recrystallizes and ages. Sensors must be then renewed and re-labeled occasionally. Reliable combinations of materials used for thermocouples are available in the literature.

## 2.2.2 Metals and alloys used for thermoelectric couple fabrication

**Thermoelectric couple** consists of two conductors from dissimilar materials electrically connected at one end – this is the sensor part. **Heating of this part** generates **thermoelectric voltage** at the “cold” contact part.

**Thermoelectric voltage** depends on the **material** and the **temperature difference**  $\Delta T$  between sensor and cold contact.

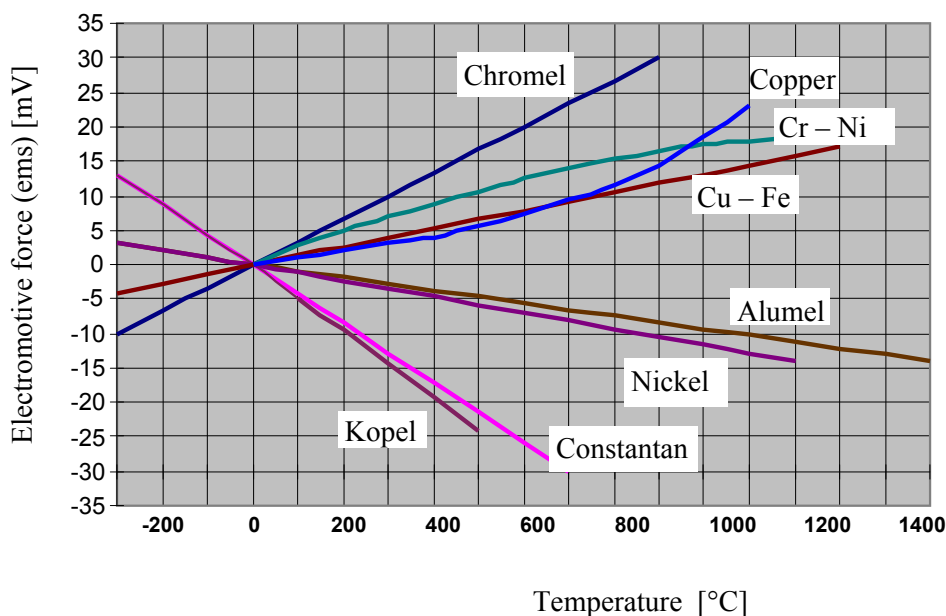
**Requirements:** high accuracy (mV/K), stable dependency of thermoelectric voltage, linear or approximately linear dependence of  $\Delta U = f(\Delta T)$ , good mechanical properties, chemical resistance, thermal resistance and long-term stability of properties of the material.

**Alloy types:** Cu; Fe; Ni; Pt; 50 % Ni + 50 % Cr; 87.5 % Ni + 12.5 % Cr; 84 % Ni + 16 % Mo; 56 % Cu + 44 % Ni (**kopel**); 90 % Ni + 10 % Cr (**chromel**); 95 % Ni + Al + Mn + Si (**alumel**); 90 % Pt + 10 % Rh; 94 % Pt + 6 % Rh; 70 % Pt + 30 % Rh ...

**Application:** temperature measurements and direct conversion of heat to electricity (some semiconductors).

**Table 2.2** Chemical composition, mechanical properties and resistivity of some thermocouple materials for low and medium temperature measurements

| Ni alloys       | Chemical composition [wt. %] |      |        |         |      |       |         | Mechanical properties |         |         | Resistivity [ $\mu\Omega\text{cm}$ ] |
|-----------------|------------------------------|------|--------|---------|------|-------|---------|-----------------------|---------|---------|--------------------------------------|
|                 | Ni                           | Fe   | Si     | Mn      | Cu   | Cr    | Al      | $R_m$ [MPa]           | $A$ [%] | HB      |                                      |
| Chromel (ch)    | balance                      |      |        |         |      | 9÷10  |         | 60÷70                 | 35÷45   | 150÷200 | 60÷70                                |
| Alumel (a)      | balance                      |      | 0.85÷2 | 1.8÷2.2 |      |       | 1.8÷2.5 | 56                    | 36      | 130     | 25÷35                                |
| Constantan (ko) | 40                           |      |        | 1.5     | bal. |       |         | 40÷50                 | 30      | 80÷90   | 48                                   |
| Kopel (k)       | 43                           |      |        | 0.5     | bal. |       |         | 40                    | 35      | 85÷90   | 49÷50                                |
| Nichrom Ch20N80 | 75÷78                        | bal. |        |         |      | 20÷23 |         | 70                    | 50      |         | 115                                  |
| Nichrom Ch15N60 | 55÷61                        | bal. |        |         |      | 15÷18 |         | 64                    | 28÷30   | 180÷230 | 110                                  |



**Fig. 2.4** Temperature dependence of electromotive voltage of chosen metals, relative to platinum

## TEMPERATURE RANGES:

Medium-high temperatures (oxidation environment):

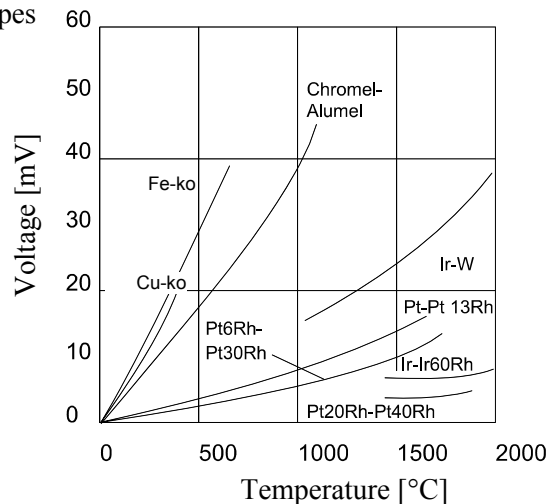
0 ÷ 1500 °C                      thermocouple Pt – Pt 90Rh10 (resp. Pt –Pt80Rh20)  
 0 ÷ 1700 °C                      thermocouple Pt70Rh30 – Pt94Rh6 (thermoelectric voltage  $\approx 11.5 \mu\text{V}\cdot\text{K}^{-1}$ )

Very high temperatures:

W95Re5 – W74Re26  
 W97Re3 – W74Re26  
 Ir – Ir40Re60

**Table 2.3** Technical labelling (standard) of some thermocouple types

| IEC 584          | Composition      | Temperature range [°C] |
|------------------|------------------|------------------------|
| <b>T</b>         | Cu-CuNi, Cu-ko   | - 200 to 350           |
| <b>J</b>         | Fe-CuNi          | - 200 to 750           |
| <b>E</b>         | NiCr-CuNi, ch-ko | - 100 to 900           |
| <b>K</b>         | Ni-CrNi, ch-a    | - 200 to 1200          |
| <b>N</b>         | NiCrSi-NiSi      | - 200 to 1200          |
| <b>S</b>         | PtRh10-Pt        | 0 to 1600              |
| <b>R</b>         | PtRh13-Pt        | 0 to 1600              |
| <b>B</b>         | PtRh30-PtRh6     | 300 to 1700            |
| <b>DIN 43710</b> |                  |                        |
| <b>L</b>         | Fe-CuNi, Fe-ko   | - 200 to 900           |
| <b>U</b>         | Cu-Ni, Cu-ko     | - 200 to 600           |



**Abbreviations:** ko – constantan, ch – chromel, a – alumel.

**Fig. 2.5** Comparison of accuracy and temperature ranges of chosen thermocouples

## 2.2.3 Construction design of thermocouples

### Measurement circuits with thermocouples

Circuit examples:

- circuit consisting of thermocouple and computing device,
- computing device with internal compensation has the cold contacts connected to its terminals. This circuit is commonly used, if the computing device can be placed close to the measured area;
- circuit consisting of thermocouple, compensation line and computing device,
- circuit consisting of thermocouple, compensation line, compensation box or thermostat for compensation line and the copper line, computing device;
- circuit consisting of thermocouple, double line converter placed in the head of the temperature sensor unifying the output signal, copper line and computing device,
- circuit consisting of thermocouple, compensation line, double line converter placed outside the sensor (on a wall or a lath) unifying the output signal, copper line, computing device,
- circuit consisting of thermocouple, terminal with temperature sensor connected to the converter, double line converter unifying the output signal, copper line and computing device.

### Wire thermoelectric couples

Wire thermocouple consist of two metal conductors placed in insulating bushings. The bushings facilitate protection against environment and, more importantly, electrical insulation. Depending on the temperature range, the material of bushings can be plastic, glass, ceramic, etc. Ceramic bushing, double or quadruple capillary configuration is common for industrial purposes. The protection can be further increased by placing the thermocouple in one or two (inner, outer) protective tube made either both from ceramics or inner metallic and outer ceramic, closed from one side. Wire thermocouples are usually fabricated from noble metals S or B type with 0.5 to 0.35 mm diameter and from common metals of J, (L) and K type with bigger outer diameter, for example 3.2 mm. For special purposes, wire thermocouples (e.g. K type) with wire diameter of hundreds or even tens of micrometers are used.

### Thermocouples from plated cable

Thermoelectric couples from plated cable with inorganic insulation, also known as plated thermocouples (PT) have been used for many years. The lines (conductors) of these thermocouples are placed in dense inorganic insulation (usually MgO or Al<sub>2</sub>O<sub>3</sub>) - the top metallic cover has tubular shape. Outer diameter of this cover (tube) is

0.25 to 12 mm. Plated cable usually contains two, four or six lines, effectively forming single, double or triple thermocouple. Less common setup with, for example, T type thermocouple (Cu-ko) has one wire conductor, the other conductor is facilitated by the cover. The tail of the conducting cover can be insulated, grounded or opened.

These thermocouples can be fabricated from common metals, for example J, (L), K type but also from noble metals (S, B). The N (NiCrSi-NiSi) thermocouple is becoming popular; its main advantage, compared to the similar K-type thermocouple, it is better stability at elevated temperatures.

## 2.2.4 Semiconductor thermoelectric converters

Several important attributes need to be defined before we can characterize the thermoelectric converters.  $Z$  [K<sup>-1</sup>] parameter is defined as an efficiency factor of thermoelectric converter;  $ZT$  is defined by equation:

$$Z = \frac{S^2 \sigma}{\lambda} \quad \text{and} \quad ZT = \frac{S^2 T \sigma}{\lambda}$$

The  $S$  [V·K<sup>-1</sup>] is Seebeck coefficient (thermoelectric sensitivity),  $T$  [K] is thermodynamic temperature,  $\sigma$  [S·m<sup>-1</sup>] is electric conductivity and  $\lambda$  [W·m<sup>-1</sup>·K<sup>-1</sup>] is thermal conductivity.

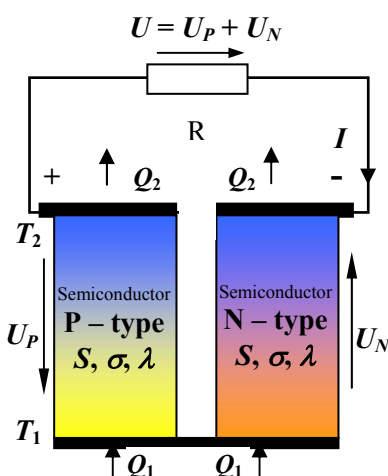
Metals are usually poor thermoelectric materials since they exhibit low Seebeck coefficient and their high thermal conductivity is mostly electron based. Insulators have high Seebeck coefficient and low electron conductivity but also very low electric conductivity. Semiconductors are therefore the best material for thermoelectrics, with their properties somewhere between metals and insulators.

**Thermoelectric cooling** employs the Peltier effect – thermal gradient occurs in material when subjected to electric or magnetic field. Electric field causes electron in material to move in unified motion – this is basically an energy transport which exhibits as current flowing from the positive to the negative terminal and thermal gradient between the two terminals.  $Z$  sums up the essential properties of the thermocouple. Industrial thermocouples have  $Z = 1.5 \div 3 \cdot 10^{-3} \text{ K}^{-1}$ ,  $Z$  of laboratory thermocouples is usually higher. Table 2.4 shows the characteristics of some semiconductor thermoelectric materials.

**Table 2.4** Properties of semiconductor thermoelectric materials

| Temperature range [K] | Semiconductor composition   | Doping element | Type of conductivity | $S$ [ $\mu\text{V}\cdot\text{K}^{-1}$ ] | $\rho$ [ $\Omega\cdot\text{cm}$ ] | $\lambda$ [ $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ] | $Z$ [ $\text{K}^{-1}$ ] | $ZT$ |
|-----------------------|---|----------------|----------------------|---|-----------------------------------|--|-------------------------|------|
| 300 ÷ 500             | 75 % Sb <sub>2</sub> Te <sub>3</sub> + 25 % Bi <sub>2</sub> Te <sub>3</sub> | Te, Se         | P                    | +200                                    | $8.5 \cdot 10^{-4}$               |  | 0.0033                  |      |
|                       | 85 % Bi <sub>2</sub> Te <sub>3</sub> + 15 % Bi <sub>2</sub> Se <sub>3</sub> | I              | N                    | -200                                    | $10^{-3}$                         |  |                         |      |
| 300 ÷ 500             | 95 % GeTe + 5 % Bi <sub>2</sub> Te <sub>3</sub>                             |                | P                    |   |                                   |  | 0.0017                  | 1.3  |
|                       | 75 % PbTe + 25 % SnTe   |                | N                    |   |                                   |  | 0.0018                  |      |
| 800 ÷ 1200            | 70 % Si + 30 % Ge   | B              | P                    | +130                                    | $10^{-3}$                         | 0.06   | 0.08                    | 0.85 |
|                       | 70 % Si + 30 % Ge   | As or P        | N                    | -160                                    | $1.6 \cdot 10^{-3}$               | 0.06   | 0.095                   | 1.1  |

**Thermoelectric converter** resp. **Peltier couple** is power source converting the heat to electricity by Seebeck thermoelectric effect. Schema of thermoelectric converter setup is shown on Fig. 2.6.



Thermoelectric converter consists of two different semiconductors – one is P-type, the other is N-type. Semiconductors are joined at one end by a bridge (heat  $Q_1$  input point) to the thermo-converter (hot contact, thermodynamic temperature  $T_1$ ). The other side of the semiconductor has metallic contacts which work as cooling surfaces for removing the  $Q_2$  heat from the converter (cold contact, thermodynamic temperature  $T_2$ ) and also facilitating the circuit contact terminals. Thermoelectric voltage is generated in the opened circuit and the output power is consumed by the connected resistor – Fig. 2.6. Efficiency and output of the converter depends on the material (semiconductor), dimensions of the semiconductor rods and the resistance  $R$  of the resistor. Material also determines the maximum allowable temperature  $T_1$ . The basic characteristic of the converter according to Fig. 2.6 are: diameter and length of the rod, resistivity  $\rho_N, \rho_P$ , Seebeck coefficients  $S_N, S_P$  and thermal conductivities  $\lambda_N, \lambda_P$ .

**Fig. 2.6** Principle of semiconductor conductor



Thermoelectric converters can also directly convert heat to electricity. They are being employed as alternative new-generation power sources to some extent, mostly as a part of systems, where internal heat flow with high temperature gradient is present. These are suitable for long-term operation (tens of years, space travels or cathodically attacked gas line protection).

**Thermoelectric generator** usually consists of P and N type semiconductor with temperature gradient between them. These components are connected in series electrically and in parallel thermally. By connecting some kind of appliance to the generator circuit, electrical power is produced. Combination of P and N-type semiconductor generates the highest powers and voltages. The Seebeck coefficients for P and N-type semiconductor have opposite signs – this effectively doubles the thermoelectric performance power – Fig. 2.6. For effective energy conversion, high thermoelectric coefficients but also high electric and thermal conductivity ( $\sigma$ ,  $\lambda$ ) are necessary. Combined characteristics of the thermoelectric conversion material are described by the  $Z$  efficiency factor.

The contact between metallic parts and semiconductors is crucial – the contact resistance must be low and it also has to be stable at elevated temperatures. Voltage is adjusted by connecting multiple converters in series or cascade with different semiconductor materials used along the temperature gradient (low-, medium-, high-temperature).

Basic materials for Peltier couple are bismuth-tellurides i.e. ternary Bi-Te-Se systems (N-type) and Bi-Sb-Te (P-type). These have good thermoelectric properties, low specific resistivity and low thermal conductivity. Connecting bridges are usually made of copper (low resistivity, solderable). Its main drawback is the possibility of diffusion towards semiconductor material thus worsening its properties. Contact between the bridge and the semiconductor creates unwanted contact resistance which affects maximum output  $Q$  of the couple. Even the best thermoelectric material is useless without feasible fabrication process providing low contact resistance. Couples are usually connected in series forming so called „battery powered (electro-thermal) cooler“. To achieve higher thermal gradient while maintaining the cooling performance, single thermo-components are connected in cascade – individual batteries need to be well insulated. Ceramic with good thermal conductivity is usually used for this purpose.

### Examples of semiconductor thermoelectric converter material (Fig. 2.7)

**Zn<sub>4</sub>Sb<sub>3</sub>** is an excellent thermoelectric material for the 200 to 350 °C temperature range, it is a P-type semiconductor. This material presents a bridge between performance materials Bi<sub>2</sub>Te<sub>3</sub> (P-type) which are most effective at lower temperatures, and Te/Ag/Ge/Sb („TAGS“) or PbTe (both P-type) which are very effective at high temperatures.

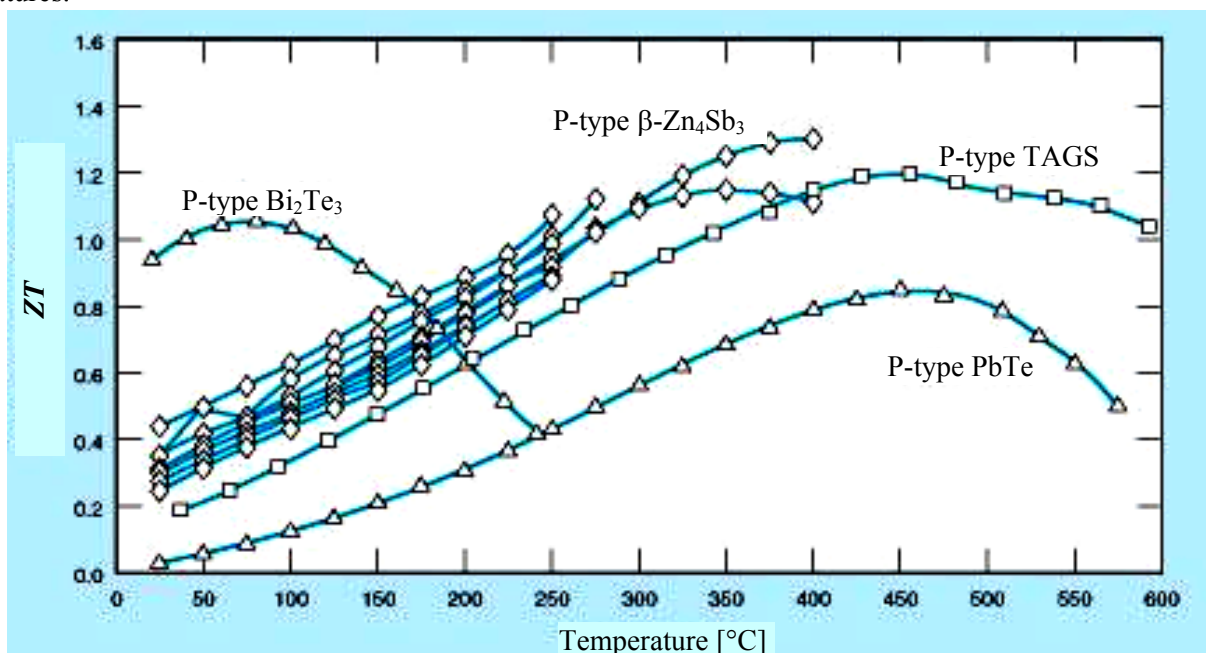
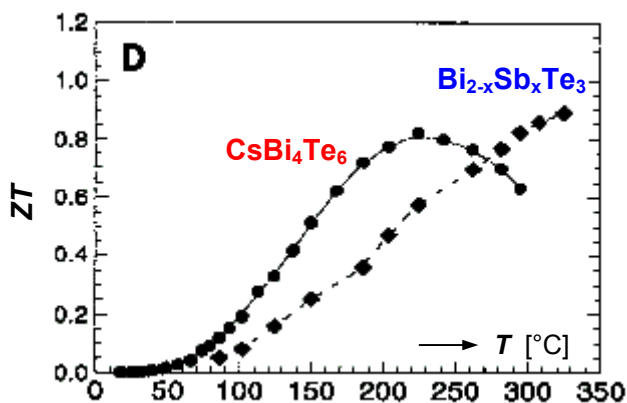


Fig. 2.7 ZT values for various semiconductor thermoelectric converters in relation to temperature

**Zn<sub>4</sub>Sb<sub>3</sub>** has three known structural modifications: α-phase is stable under –10 °C, β-phase in –10 to 492 °C range and γ-phase is stable from 492 °C to its melting point 566 °C. Zn<sub>4</sub>Sb<sub>3</sub> is therefore present as β-phase in practice with forbidden band width of 1.2 eV. β-Zn<sub>4</sub>Sb<sub>3</sub> modification is strongly doped P-type semiconductor. Interesting fact about β-Zn<sub>4</sub>Sb<sub>3</sub> is its low thermal conductivity (lower limit of only 6 mW·cm<sup>-1</sup>·K<sup>-1</sup> at 250 °C) which

also lowers the  $ZT$  values. This is the lowest thermal conductivity value of any known thermoelectric material.  $\beta$ - $\text{Zn}_4\text{Sb}_3$  has many theoretical applications in thermoelectric generators for conversion of waste heat to electricity. These are used in devices generating heat in suitable temperature range. Examples of  $\beta$ - $\text{Zn}_4\text{Sb}_3$  application are waste incinerators, geothermal power plants (including platforms mining hot oil) or cars. Fig. 2.7 compares the  $ZT$  values for various materials.

**$\text{CsBi}_4\text{Te}_6$**  – also very efficient, however the  $ZT_{\text{max}}=0,8$  at  $225\text{ }^\circ\text{C}$  – Fig. 2.8.



One of main application of thermoelectric materials is cooling systems, also known as **Pietri coolers**. Electric power conversion generates thermal difference applicable for cooling.  **$\text{Bi}_2\text{Te}_3$**  ( $ZT = 0.9$  at  $20\text{ }^\circ\text{C}$ ) is an example of such material. The compressor equipped coolers ( $ZT = 3$ ) are still much more effective than these materials. However, Pietri coolers are more reliable than compressor equipped coolers. NASA employs thermoelectric materials for propulsion cooling, in cars... Other possible material combinations are for example  **$(\text{Bi,Sb})_2\text{Te}_3$**  (P-type) and  **$\text{Bi}_2(\text{Te,Se})_3$**  (N-type).

Fig. 2.8 Comparison of  $ZT$  for  $\text{CsBi}_4\text{Te}_6$  and  $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$

### Si - Ge based thermoelectric materials

Micro-alloyed **Si - Ge** with varying Si:Ge ratio is another perspective material. Combination of Si alloyed with 5 at. % Ge doped with 0,3 at. % B or 0,4 at. % P can decrease the thermal conductivity by 5.7 or 6.7 % compared to pure Si (at 298 K). Seebeck coefficient  $S$  of doped Si has local maximum at charge carrier concentration of  $(3\div 4)\cdot 10^{19}\text{ cm}^{-3}$ , while in doped  $\text{Si}_{0,97}\text{Ge}_{0,03}$ , such maximum has not been observed. Thermoelectric efficiency  $ZT$  of  $N$ - and  $P$ -type  $\text{Si}_{0,95}\text{Ge}_{0,05}$  increases linearly with temperature  $T$  and values of  $ZT = 0.90$  and  $0.57$  at  $1073\text{ K}$  have been measured.

### **$\text{La}_{0,9}(\text{Sr}_{1-x}\text{Ca}_x)_{1,1}\text{CoO}_4$**

Conducting characteristics and promising magnetic properties predetermine polycrystalline ceramic materials of  $\text{La}_{0,9}(\text{Sr}_{1-x}\text{Ca}_x)_{1,1}\text{CoO}_4$  type for thermoelectric application.

Thermoelectric properties of  **$\text{CoSb}_3$**  can be further enhanced by Ni, Pd and Pt doping (donor additives). Hall mobility, Seebeck coefficient and electric conductivity are strongly affected not only by donor concentration but also by impurities. High thermoelectric efficiency value  $ZT = \text{around } 0.85$  (at  $800\text{ K}$ ) was achieved by doping by both Pd and Pt.

## 2.3 SOLDER MATERIALS

**Solders** are alloys used in liquid state to firmly connect two metals. In principle, the solder wets the surface of the metals, enters their structure and forms firm connection during solidification. The connected metals do not melt during this process. Good adhesion between the solder and the metal is crucial. Many physical, technological and mechanical properties determine their overall function. Unlike during welding, soldering is a diffusion connection facilitated by added material and **flux** mixture melted at temperatures lower than melting points of both metals. The purpose of the flux is to remove the oxide layers on the soldered surfaces. Use of protective atmosphere (e.g. argon, nitrogen) aids the process by protecting the surfaces against oxidation. Alternatively, gasses with high oxygen affinity can be used: mixture of nitrogen with hydrogen as a reactive substance. Soldering materials are produced in the form of strips, foils, rods, wires and also tubes with flux inside them, cast rods and grains.

### Basic requirements for solders:

- good thermal and electric conductivity,
- low soldering temperature,
- good wetting properties,
- high mechanical strength of the joint,
- corrosion resistance of the joint.

Solder must always have **lower melting point than the soldered metals**.

**Soldering interval** for capillary soldering must be **narrow** (< 100 °C); alternatively, **eutectic composition** solder can be used. Otherwise, the alloy components (with lower melting point) tend to separate, especially during slow heating. The lower melting point component of the eutectic solder melts first and leaves skeleton of the higher melting point component (solid solution). This phenomenon is called **liquation**; and its highly undesirable during soldering. Forming skeleton is not fluid and the solder therefore cannot fill the gap between metals completely. Solder with wide melting interval (> 100 °C) has even worse capillary soldering properties. Although it can be used as a deposited solder.

Solder and the soldered metals **cannot form alloys with significantly lower melting point**.

Solder, unlike welding wire does not necessarily need to have same chemical composition as the soldered metals.

**Good soldering properties** are necessary for quality capillary soldering (wetting, fluidity, capillary attraction).

These properties depend on chemical composition of the solder and also on used flux. For deposited soldering, good wetting properties are sufficient.

Impurities in the solder severely deteriorate the deformation properties of the joint, as well as its corrosion resistance. **Highly pure materials** are therefore desirable for their production.

The solder components must have specific **solubility and diffusive ability**, without forming brittle intermediate phases. This is, however, determined by the combination of the solder and base metal, temperature and soldering time.

Liquid solder must have low **surface tension** and **low viscosity**. These are again determined by the chemical composition and soldering temperature.

The joint and the base metal can be attacked by galvanic corrosion, so a solder with **similar electrochemical potential** is required.

Solder needs to have **good mechanical properties** (shear, tensile strength, ductility, and also hardness), but most importantly must be able to form **firm joints**. This is also determined by the chemical composition and quality of the diffusion part of the joint (its composition).

Pure metals generally have good soldering properties, high ductility but low strength. Eutectic solders have similar properties with higher hardness, strength and brittleness. Solders with high malleability, yet lower strength, are suitable for short-term high-load joints. High load causes brittle joints to crack.

Process technology also dictates to use suitable **shape of the solder**. Appropriate type of solder is chosen according to these criteria:

- a) type of soldered metals and solder construction,
- b) available soldering technology,
- c) operation requirements, resp. type of loading (tensile, shear, shock, fatigue, creep, corrosion, oxidation etc.),
- d) economy of the production.

**Solders can be divided, by their melting point, to:**

- a) **Easy-melting (up to 200 °C)**      b) „Soft” solders (200 – 500 °C)      c) „Hard” solders (over 500 °C)

With the border at **500 °C**, solders are either soft or hard. **Soft** solders are then divided to **tin solders** and **special solders**; **hard solders** are divided to **aluminum, copper** and **silver solders**. There is a large variety of commercial solders for temperatures up to 350 °C. Soft solders are metal alloys with low melting points, e.g. Sn, Pb, Cd, Sb and Bi. Gold diffusion solder can be used for demanding applications. Above 1000, resp. 1500 °C, there are not many solders available, since the number of metals with sufficiently high melting point is low. Solders for electrical engineering have different properties and belong to the group of **special solders**. Use of highly pure raw materials is typical. Soldering by flame is rare, **capillary soldering** is preferred.

### **2.3.1 Low-melting solders**

Usually binary or ternary multi-component alloys of Pb-Bi-Sn-Cd with composition close to the eutectic point. Some of the alloys have their own name, e.g. **Wood’s metal** with melting point of 68 °C and **Rose’s metal** with melting point at 94 °C. Addition of indium lowers the melting point of Wood’s metal to 47 °C. Solder of gallium with 8 % of Sn melts at 20 °C, gallium solder with 24 % of indium at 16 °C. Indium and its alloys wet surface of many known metallic and non-metallic materials. **In-Cu-Ag** and **In-Cu-Au** are used for soldering of gold alloys. These materials are used for production of **thermal circuit breakers for main transformers**. Easy-melting alloys are also suitable as tube filling (e.g. waveguide fabrication) before their bending, for temperature measuring purposes (melting of the metal indicates that desired temperature has been reached) and for investment casting.

**Table 2.5** Examples of low-melting solders, eutectic alloys composition

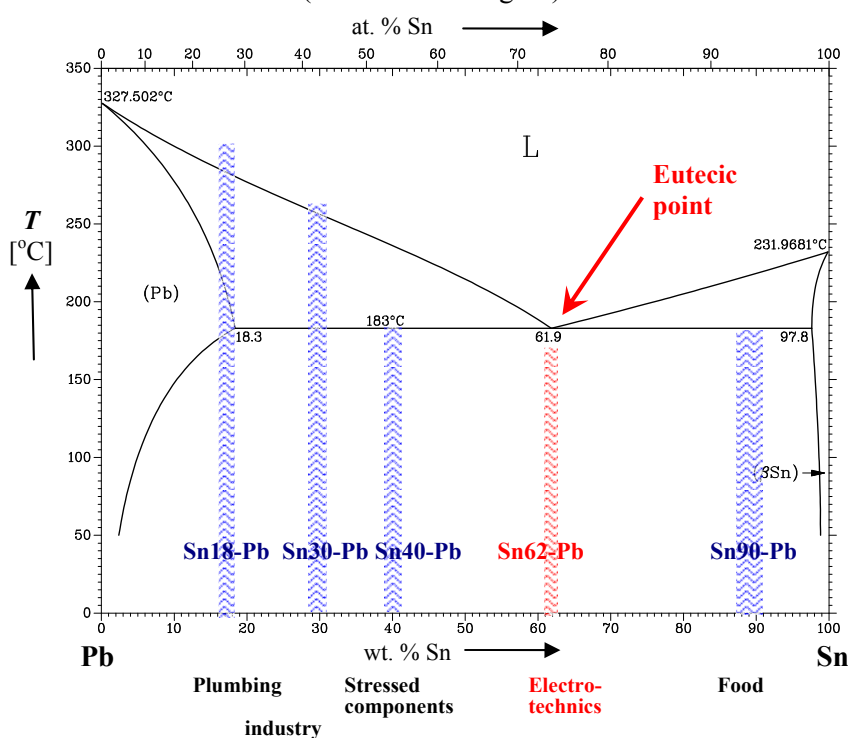
| Melting temperature [°C] | Chemical composition [wt. %] |      |      |      |         |
|--------------------------|------------------------------|------|------|------|---------|
|                          | Sn                           | Pb   | Bi   | Cd   | Others  |
| 20                       | 8                            | -    | -    | -    | Ga 92   |
| 47                       | 10.6                         | 22.0 | 41.1 | 8.2  | In 18.1 |
| 68 <sup>*)</sup>         | 12.9                         | 27.6 | 49.5 | 10.0 | -       |
| 91.5                     | -                            | 40.2 | 51.7 | 8.1  | -       |
| 94 <sup>**)</sup>        | 16                           | 32   | 52   | -    | -       |
| 102.5                    | 25.9                         | -    | 53.9 | 20.2 | -       |
| 124.3                    | -                            | 44.5 | 55.5 | -    | -       |
| 138.5                    | 43                           | -    | 57   | -    | -       |
| 183.3                    | 61.9                         | 38.1 | -    | -    | -       |
| 199                      | 91                           | -    | -    | -    | Zn 9    |
| 236                      | -                            | 79.7 | -    | 17.7 | Sb 2.6  |
| 247                      | -                            | 87   | -    | -    | Sb 13   |

<sup>\*)</sup> Wood's metal, <sup>\*\*)</sup> Rose's metal

### 2.3.2 Soft solders

Soft solders, in fact, alloys with low-melting point – typically tin and lead alloys are used for joining copper, brass, zinc, lead but also steel. Solders with less than 20 % of tin are harder to melt, **flame melting** is usually employed. Solders with over 30 % of tin are suitable for plumbing. Alloys with more than 90 % tin are heated with **flux** and are typically used in electrical engineering. Effort to reduce tin content gave rise to solders with tin partially or completely replaced with other elements. **Pb-Sn-Cd** solder has tin partially replaced with cadmium. Solders **Pb-Sb** and **Pb-Ag-Cu** are tin-less. **Sn-Zn** and **Cd-Zn** are used for soldering of aluminum. Solders with more than 60 % of tin have highest strength and hardness.

Soft solders containing lead have two main applications: **electrical engineering** and **heat exchangers**. From ecological point of view, lead in soft solders and cadmium in hard solders are the biggest issue. Alternative, **lead-free solders** are soft solders with high content of Sn and low amounts of Ag, Cu, Bi, Sb, Zn, In, Mg; their composition is eutectic. Lead-free solder usually requires higher temperatures. Most of these alloys are utilized as soft solders. In the group of eutectic binary solders, only the alloys with high content of bismuth (58 %), indium (52 %) and gallium (86,5 %) have lower melting point. Application of these alloys is limited by their higher price, insufficient reserves and unclear availability. Of course, ternary eutectic alloys, such as **SnAg3.5Cu0.7**, with melting point or quaternary tin alloys can be used. Melting points of these alloys is however always higher than common Sn-Pb solders (at least 30 °C higher).



**Fig. 2.9** Binary Pb-Sn system – eutectic point is highlighted, regions of significant of Pb-Sn solders

**Note:** Element contents are always noted in [wt. %] for practical reasons unless stated otherwise.

## Soft solders for automated soldering

For automated soldering in electronics, solders derived from eutectic Sn-Pb alloy are utilized (61.9 % of Sn and 38.1 % Pb) – see Fig. 2.9. Eutectic temperature is 183 °C. Nowadays, alloys with composition slightly below eutectic point (60 % Sn) are preferred. Tin is partially replaced with cheaper bismuth. This alloy is very suitable for automated soldering. Modern process uses the **standing wave principle** – large amount of solder is melted and stationary wave is created by pumps. Printed board circuits are moved through the ridge of the wave. The solder is not immediately used as in hand welding, and it stays in contact with the atmosphere. The impurities accumulate in the solder and the solder reacts, forming oxide layer on the surface. This can be prevented by adding soldering oil. Impurities have detrimental effect on the wetting and mechanical properties of the solder. Joint loses its gloss and dendrites begin to appear. The solder hardness increases but also becomes brittle. The chemical composition of the solder needs to be monitored – especially the concentration of **solder inhibitors** - zinc, cadmium, iron and aluminum.

**Tin solders** are Sn-Pb alloys with soldering temperature of 190 to 350 °C. Tin is the functional component and provides good wetting properties. Tin concentration has strong effect on soldering quality. Lead, on the other hand, has poor wetting properties and does not react with the base metal. Even small amount of tin (min. 3 %) or other surface-active element (Sb and others) is sufficient to substantially enhance the soldering properties. Tin solders contain 4 to 90 % of tin.

Electric conductivity of tin solders is about 10 to 5 % of copper; conductivity increases with higher tin content. Sn50Pb and Sn60Pb have the best soldering and mechanical properties.

**Wetting properties** – the ability to maintain contact with soldered metal, **capillary attraction and fluidity** determine the **quality of the joint**. These attributes depend on the alloy type, impurities and gas concentration, as well as soldering temperature. Pure metals and eutectic solders have the best fluidity. Shear and tensile strength are the most important mechanical properties of the joint.

### **Soft Sn-Zn solder (for aluminum soldering)**

- labeled Sn70-Zn, composition of 69 % to 71 % Sn, balance Zn, upper and lower melting point 315/200 °C, tensile strength of the soldered joint 60 MPa, shear strength of 40 MPa. Application examples: soft soldering of thin aluminum sheets and foils. Usually soldered without flux or with **stearin** addition.

### **Soft Pb solder**

- Pb-Ag<sub>2,5</sub>-Cu, composition of 2 to 3 % Ag + 0,2 to 0,3 % Cu + balance Pb, melting point: upper limit of 350 °C and lower limit of 295 °C. Tensile strength of 40 to 45 MPa, shear strength 35 MPa. Used for soldering in the electrical engineering.

## Lead-free solders

Many aspects need to be considered while proposing new solder. The solder joints must be highly conductive in both heat exchangers and in electrical engineering applications. Good fluidity and ability to fill the cavities in the joint, so it is not gas-penetrable is necessary for heat exchangers, radiators and water pipelines. Electric conductivity is important for application in electric engineering, thermal conductivity for heat exchanger manufacture. Another aspect, especially for electronic application, is low melting point – this prevents damage of the circuit board or components during soldering. Alloy components must be available in sufficient amounts, also must be environment-friendly, non-toxic and of course reasonably costly.

For reasons mentioned above, the Sn-Pb solders are being slowly replaced by other tin-based alloys. Numerous lead-free tin binary alloys have been proposed. Alloys with eutectic or close to eutectic composition have been chosen for their narrow solidification interval. Alloys **99Sn1Cu**, **97Sn3Cu**, **96.5Sn3.5Ag**, **95Sn5Sb**, **91Sn9Zn** and **42Sn58Bi** are time-proven. Important attributes of these alloys are wetting properties, melting point, mechanical properties and also resistivity.

**Wetting** is defined as an ability of liquid solder (flux) to establish contact with clean surface at given temperature. **Fluidity** is the ability of liquid solder (flux) to spread across the surface of the base material at given temperature. The only condition required from all solder alloys is good wetting of the substrate. Wetting is closely related to the surface tension between the interfaces. Inter-atomic forces form bonds across the interface which quickly spread across the whole contact area. Formation of intermetallic compound is necessary condition for good wetting properties and firm connection between the solder and the metal. **Intermetallic compounds** can still form after the weld joint has solidified (under melting point) – for example by atomic diffusion.

All tin-based solders react with copper, iron and nickel forming **intermetallic compounds** at interface. With copper, tin solders react forming intermetallic phases **Cu<sub>3</sub>Sn** and **Cu<sub>6</sub>Sn<sub>5</sub>** at interface (Cu<sub>3</sub>Sn closer to Cu substrate and Cu<sub>6</sub>Sn<sub>5</sub> in contact with the solder) and sometimes also in the solder.

**Table 2.6** Summary of properties of lead-less solders in relation to Sn-Pb solders

| Solder         | Melting point [°C] | Substrate wetting properties |   | Strength [MPa] | Resistivity [ $\mu\Omega\cdot\text{cm}$ ] | Reaction rate |
|----------------|--------------------|------------------------------|---|----------------|---|---------------|
| <b>SnPb37</b>  | 183                | Good                         | B | 21.0           | 0.1427                                    | Middle        |
| <b>Sn</b>      | 232                | Good (0)                     | B | 19.5 (0)       | 0.1106 (+)                                | Fast          |
| <b>SnCu1</b>   | 227                | Perfect (+)                  | A | 20.0 (0)       | -   | Middle        |
| <b>SnCu3</b>   | 227÷310            | Perfect (+)                  | A | 18.8 (0)       | 0.0990 (+)                                | Middle        |
| <b>SnAg3.5</b> | 221                | Good (0)                     | B | 20.6 (0)       | 0.0891 (+)                                | Middle        |
| <b>SnSb5</b>   | 235÷245            | Good (0)                     | B | 22.8 (0)       | 0.1471 (0)                                | Fast          |
| <b>SnZn9</b>   | 199                | Slow (-)                     | C | 19.0 (0)       | 0.0959 (+)                                | Fast          |
| <b>SnBi58</b>  | 138                | None (-)                     | D | 22.1 (0)       | 0.4145 (-)                                | Slow          |

(+) better than SnPb37 (0) similar to SnPb37 (-) worse than SnPb37

### Soft solder flux

is soldering additive for metal joining. In electronics, flux additive is especially important for automated soldering. Fluxes affect not just the joint quality, its residues also influence the stability of printed circuit board and soldered joints connection, especially in wet environments. Flux cleans the surface of oxides, nitride and damaged coatings containing impurities – this way, uncovered lattices of the metals are achieved which can then form good joint. Fluxes for soft soldering are traditionally **aggressive or mild**. Aggressive fluxes contain salts, acids or organic halogen compounds and strongly increase the quality of soldered joints. They easily dissolve metal oxides and uncover the lattice. However its residua can corrode the joint. Mild fluxes react slower, but don't cause corrosive attack. **Rosin**, containing only traces of ionic contaminants had been recommended for demanding soldering tasks until detailed understanding of the corrosion processes.

Flux F-TAm is so called self-activated new generation flux for automated **soft soldering by wave** in protective atmosphere. It consists of exclusively synthetic organic material of defined composition and pure water. Flux, without any halides and without any alkali or metal ions typically has of pH 6 to 6.5. The flux has high wettability without an organic thinner, it is characteristic for mobility of its functional compounds. Its efficiency increases with soldering temperature.

### New soldering technologies

Nowadays, electronic devices are usually fabricated from printed board circuits with holes and terminals for other electronic components which are then machine-soldered on it using solder and flux. Terminal materials are made of various metals and are usually plated with nobler metal which increases their solderability and climatic resistance. Each fabrication process has different features. Wetting properties and resistance in given environment are the parameters with greatest impact.

Dynamic development in electronic and especially microelectronic industry helped to develop various new technologies including the laser soldering of electronic components to already densely populated (by components) board circuits. Solid state Nd:YAG lasers were used for soldering at first, to prevent absorption of the light in the flux material. Other than that, strong diode lasers are becoming popular nowadays.

### Ultrasounds soldering

The soldered place, along with melted solder is subjected to mechanical oscillation of 5 to 100 kHz which disintegrates the surface oxide layer and allows the metals to be connected. Ultrasound soldering is facilitated by either submerging into bath or local soldering. The solder is firmly connected to the magnetostriction oscillator (nickel sheet) which generates heat. Current, produced in special generator, flowing through the wiring oscillates the sheet; the solder is heated by eddy currents.

### 2.3.3 Hard solders

Solders with melting point over 500 °C (also called hard solders) are used for soldering of copper, steel, cast iron, nickel, etc. Metals and alloys with higher melting point can be joined using hard solders. Hard soldered joints can be operated at higher temperatures, have high toughness, fatigue and corrosion resistance – these outline their application.

Typical hard solder materials are **brass solders with addition of nickel, silver** and other elements, e.g. standardized solder **Ms60-Ag** (melting point 870 to 900 °C), **MsNi8, Ms60-Si-Sn** and so on. **Silver solders** with lower silver content are used for soldering larger pieces of copper, its alloys and also low-carbon steel. **Silver solders** have lower temperature than brass solders, the joints have good mechanical properties and are chemical-resistant. **Hard aluminum solder** (Al-Si alloy) is typically used for aluminum soldering. Cu-Ni or pure copper is frequently used for sintered carbides and steel soldering.

Hard solders are produced from raw materials with at least 99.99 % purity. They are melted in vacuum and therefore don't contain oxides. Hard soldering is strictly without flux, in vacuum or protective atmosphere. Hard solders for electro-vacuum devices can't contain even traces of metals with vapor pressure over  $1.33 \cdot 10^{-5}$  Pa at 400 to 550 °C. Available, depending on the alloy, in form of castings, wires and powders. Noble metal solders, for example **palladium solders** have outstanding soldering properties.

#### Basic characterization of hard solders

- a) **Brass solders** - e.g. brass **Ms54**. For copper, brass, cast metal and steel soldering.
- b) **Aluminum solders** - alloys with high amount of aluminum, most often **Al-Si** alloys with other alloying elements. Joints have poor corrosion resistance.
- c) **Silver solders** various amounts of silver. For hard soldering, pure silver, **Ag-Cu** and **Ag-Cu-Zn** are often employed. Used for soldering of nickel, copper and their alloys.
- d) **Gold solders** – consist of gold with silver, copper, nickel for gold soldering. **Au-Cu** alloy is typical for vacuum electrical engineering.
- e) **Platinum solders** – platinum and silver alloys.
- f) **Palladium solders** palladium with silver, copper, also with nickel and manganese.
- g) **Hard solders for very high temperatures**

#### Brass solders

Most common hard solders are from copper and its alloys. Brass solders (copper also belongs to this group) are used for steel soldering in protective atmosphere. Increasing the zinc content decreases the melting point, but solder becomes brittle. Therefore, brasses with more than 65 % Zn are not recommended. Slow heated brass solder develops pores – zinc is evaporated and the chemical composition changes. Phosphorus copper solder Cu-P8 is recommended for soldering of brasses with more zinc; its melting point is low even without flux (710 °C). Nonetheless, this solder is unsuitable for steel soldering, because the joints are brittle. Brass solders with added silver increases their fluidity and adhesion, while keeping the porosity low. Therefore, the **Ms-60 Ag** is frequently used. Alloy with added nickel has high strength and toughness. Brass solders are suitable for welding of small components with similar shape made of for example: steel, cast iron, copper and its alloys, and for soldering of plates from sintered carbides.

#### Silver solders

Silver solders have favorable properties – generally lower melting point, higher strength and toughness and corrosion resistance. The amount of silver in the alloy also changes its color which is utilized in jewellery. Common solders contain up to 65 % of Ag. Alloys with more silver exhibit lower melting points, increased toughness and electric conductivity.

Silver solder characteristic: relatively low melting point, forms tougher and stronger joints, more chemically stable than brass solders. Silver solders with phosphor addition are suitable for copper alloys that require low soldering temperature. Solder with suitable combination of Ni, Mn and Ag forms very strong joints suitable even for soldering of corrosion-resistant steel. Cd addition lowers the soldering temperature, the joints are stronger while keeping their toughness.

Silver solders are viable for soldering of copper and its alloys, nickel and nickel alloys, steel, corrosion resistant steel, cast iron and grey cast iron, sintered carbides, metal ceramics, tungsten, tantalum, molybdenum and titanium.

Viable even for large components and joints. Utilized for soldering of Cu tubes with high current throughput and high mechanical and thermal stresses (Cu crystallizer in plasma and arc furnaces).

### Gold solders

Gold has, either as solder or as an alloy with other elements, unique properties. Its main asset is the fact that its surface does not oxidize. Soldered joint is corrosion resistant and can withstand high temperature changes; it also has very high ductility. Gold is used as diffusion solder. In form of foil or wire, copper/copper plated components be diffusive soldered at temperature around 450 to 550 °C, that is in temperature range, where only a few other solders can be used. Soldered joint is stable up to 800 °C. **Gold micro-wires** with aluminum sputtered substrate can be also diffusive soldered this way. This procedure is employed for most of the semiconductor chips with terminal contact joints.

Eutectic alloy **AuSn20** has soldering temperature 280 °C. It is used in form of cuts for vacuum sealed cover component joining (with gold deposited in advance), e.g. for hermetical sealing of ceramic casings. This alloy exhibits best vacuum tightness of the joint of all known soft solders while having high thermal-shock resistance. **Gold alloyed with antimony or silicon** in form of foil is used for reactive soldering of silicon chips coated with silver or gold in semiconductor and integrated circuit production. Combination of temperature and ultrasound is used to start the reaction in aerial conditions. Hard gold solders wet many soldered metals and alloys.

### Palladium solders

Palladium substantially enhances soldering properties of Ag-Cu and Ni-Mn hard solders. Soldered joints have high mechanical strength at elevated temperature, are more ductile and also have higher corrosion resistance.

The biggest asset of palladium is the inhibition effect on diffusion of Ag-Cu solders into FeNi and FeNiCo alloys. Mentioned properties along with relatively low cost of palladium and silver predetermine the palladium solders for complex, reliable and heavily thermal-loaded joints.

These solders are used for soldering FeNi and FeNiCo with copper and its alloys, titanium, zirconium, beryllium, tungsten, molybdenum and corrosion resistant steel. It is also viable for soldering of metal-coated ceramics. Soldering usually takes place in furnace with protective atmosphere without flux.

### Hard solders for very high temperatures

Solders materials with soldering temperatures over 1000 °C; 1500 °C respectively. For this purpose, only metals and carbides with high melting points can be considered, namely tantalum, niobium and platinum group metals.

For soldering at temperatures up to 2000 °C zirconium solder is typically used; it is able to satisfactorily join metals with high melting point (previously coated with rhodium). Zr-Rh system has excellent wetting properties. Best results are achieved with ZrRh25 solder at temperatures around 1500 °C.

### Hard solder fluxes

Most common flux for hard soldering is **borax** and **boric acid**. Borax dissolves oxides at lower temperature than boric acid (at about 800 °C), and can be therefore used with silver solders. Flux is typically a combination of borax and boric acid in various ratios. Use of dry borax is advised. Addition of ethanol to the borax mixture prevents the water intake by calcinated borax. Industrially produced fluxes contain strong chloride compounds (lithium chloride), potassium carbonate, silicon oxide, etc. Reaction temperature of the flux depends on the compound concentration and can be thus adjusted to the solder. Fluxes for aluminum, chromium-rich steel and silicon which form very stable oxides require use of strong alkali metals chlorides and fluorides flux.

## 2.4 MATERIALS FOR FUSES

Fuse is a **safety device**, designed to protect the circuit from over-current. During overload, the metal wire or strip is re-melted by heat generated by the current, thus breaking the circuit.

Fuse material requirements:

- High electric conductivity.**
- Low melting point.** The melting metal shouldn't spatter but rather **evaporate by the heat generated by the arc**.
- Low oxidation.** Surface oxide layer worsens the cooling rate thus changing the fuse characteristics; also reduces the diameter of the fuse element therefore also changing the current level at which the fuse breaks.



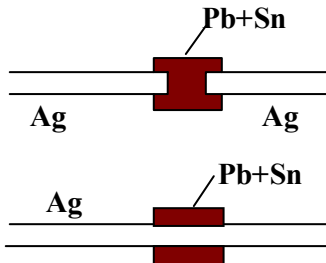
## Metals for fuse elements:

**Silver** is preferred material for the fuse element as it fits the requirements. **Copper wires** are coated with silver to prevent its oxidation or with quartz sand which also extinguishes the arc. To increase the cooling rate and the breaking capacity, the fuse element is divided in several thinner wires or strips. Some fuse elements (e.g. in devices) are made of aluminum, zinc or low melting alloys.

### Material:

High-voltage fuse: Ag, Cu, Ag + Cu (50 %)

Normal and low breaking capacity: Al, Zn, Sn + Pb



|                    |          |      |      |      |     |     |
|--------------------|----------|------|------|------|-----|-----|
| Ag wire (diameter) | $d$ [mm] | 0.06 | 0.18 | 0.47 | 1.0 | 1.4 |
| Breaking current   | $I$ [A]  | 2    | 6    | 25   | 60  | 102 |

Fig. 2.10 Principle of lowering the melting point of Ag conductors in fuses

## 2.5 METALS AND ALLOYS FOR BIMETALS

**Bimetals** consists of **two layers from different metals (or alloys)**. The layers are joined either **metalurgically** (plating, soldering) or **mechanically** (rolling). Fabricated in form of **sheets, strips** or **wires**. Divided to groups by their application purpose:

- **bend bimetals,**
- **bimetal conductors,**
- **bimetal contacts.**

### 2.5.1 Bend bimetals

Basic studied property of thermal bimetals is **specific thermal displacement** which must be high and stable with time and temperature. **Resistivity** and **operation temperature range** and **also the limit temperature** must be known for optimal use. Specific thermal displacement increases with the difference in thermal expansion of the active and passive metal. Resistivity is closely related to the type of alloys used. Thermal and electrical resistivity can be lowered by inserting interlayer of copper between the two active metals.

Bend bimetal comprises of two layers from different metals, with different coefficients of thermal expansion – Fig. 2.11. Heating the bimetal generates compressive stress in the metal with lower coefficient (**2** on Fig. 2.11) and tensile stress in the metal with higher coefficient value (**1**). Due to the stresses, the bimetal bends (Fig. 2.11c). If the temperature is the same in the whole bimetal, it forms partial circle. (Fig. 2.11c).

Bimetal couples are fabricated by shearing on a press and subsequent bending. These couples are produced in form of strips, small plates, discs, spirals or helixes. Bimetal couples are heated directly by passing current or indirectly from resistive wiring around the bimetal. Used up to 350 °C.

The metal layer with **small thermal expansion coefficient** is made of **Fe-Ni alloy with 36 to 42 % nickel** also known under name **invar**.

The metal layer with **high coefficient of thermal expansion** is made of **nickel**, **Fe-Ni alloy with about 20 % of nickel** or **Cu-Ni alloy**.

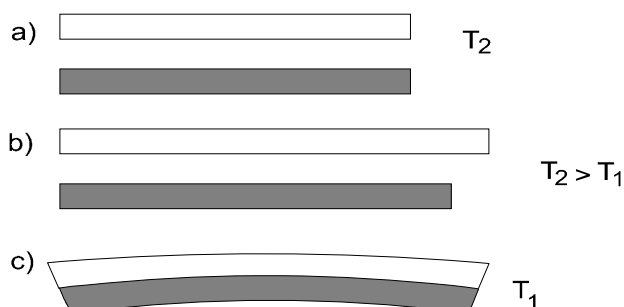


Fig. 2.11 Bend bimetal in form of a strip

a) strip before heating

b) dilatation of the two loose strips during heating

c) bimetal bends during heating

### Material solution:

### Alloys with low coefficient of thermal expansion:

**Invar** (Fe + 35,6 % Ni) -  $\alpha_l = 1.1 \cdot 10^{-6} \text{ K}^{-1}$  (fabrication of precise measuring scales, tape measure, pendulum rods and part of devices which need to be thermally stable).

**Superinvar** (Fe + 42 to 48 % Ni), coefficient of thermal expansion  $\alpha_l = 6.6 \cdot 10^{-6} \text{ K}^{-1}$  stable in wide range of temperatures  $\Delta T = 0 \div 400 \text{ }^\circ\text{C}$ .

**Covar** (54 % Fe + 29 % Ni + 17 % Co) -  $\alpha_l = (4.4 \text{ to } 5.2) \cdot 10^{-6} \text{ K}^{-1}$  in temperature range  $\Delta T = 20 \div 300 \text{ }^\circ\text{C}$ . Material for vacuum tubes, especially suitable for connection with covar glass.

**W, Mo, Ta**

**Ir, Rh, Pt** - expensive

### Alloys with high coefficient of thermal expansion:

**Nickel, iron, brass, Ni-Fe alloy**

**Alloy 20 % Ni + 6 % Mn + Fe** -  $\alpha_l = +20 \cdot 10^{-6} \text{ K}^{-1}$ .

**Important!** Thermal hysteresis: Switch off at  $T = 200 \text{ }^\circ\text{C}$ ; switch on at  $160 \text{ }^\circ\text{C}$ .

#### Application:

Bimetals are employed in large el. circuits for [switching](#) and [delayed control](#) of various circuits. Also used as [thermal fuses](#) (protection of rotary machines, transformers). Used in some devices (e.g. irons) as [thermostat](#), also in [bimetal ampere-meters and thermo-meters](#).

## 2.5.2 Bimetal conductors

Bimetal conductors can be produced by [plating](#). The base metal is joined (plated) to the base metal by rolling at elevated temperature. Produced bimetal is further worked by rolling, drawing and pressing. Semi-finished products, such as wires (so called shell wires), tubes, sheets and other.

#### Types of bimetal conductors:

- [Aluminum](#) plated from one or both sides with sheet shapes [copper](#), so called [cupal](#).
- [Iron](#) plated with wire [copper](#) for exterior media lines.
- [Iron](#) plated from both sides with sheets made of [nickel](#) (labeled N2), [aluminum](#) (P2) or with [aluminum](#) on one side and [nickel](#) on the other side (PN). N2, P2, PN sheets are used as [anodes of receiver vacuum tubes](#).
- Shell wire is from [iron-nickel](#) core and [copper cover](#). The core, with 58 % of iron and 42 % nickel determines the coefficient of thermal expansion. [Copper](#) layer on the surface can be welded with soft glass. Copper cover wire is used for metal-soft glass joints for [vacuum tubes and discharge tubes](#). Other cover wires have [copper](#) core and [nickel](#) cover or [tungsten](#) core and [copper](#) cover.

## 2.5.3 Bimetal contacts

Consist of two or more metallic layers one of them is the contact metal and the other is flexible or firm base metal. Strip along the whole length are called [overlay](#). To reduce the consumption of expensive contact metal, bimetals are nowadays fabricated just with strip of contact metal. The bimetal with strip in the same plane as the base metal is called [inlay](#); [toplay](#) protrudes from the strip surface.

First requirement for bimetal production by metallurgical processes is low temperature formability (for the fabrication of wire and profiled bimetals). [Inlay](#) can be produced galvanically or by deposition in vacuum. [Copper](#), [brass](#), and recently also [silver](#) and [Fe-Ni](#) alloys, rarely [Cu-Be](#).

[Inlay](#) is typically produced by plating – either by plating the strips and rolling, or rolling noble metal foil on the base metal in final shape. Both technologies require annealing between the steps. [Inlay](#) can be also deposited galvanically on the strip of final thickness. Strips from multiple metals can be produced by this technology. Galvanic process is viable for deposition of [gold](#) and its alloys with [Ni](#) and [Co](#), [Ag](#), [Ni](#), [Cu](#) and [Sn](#) or [SnPb](#) alloy. Galvanically deposited inlay is especially suitable for [connector](#) production. [Toplay](#) can be produced only by plating.

## 2.6 METALS AND ALLOYS FOR ELECTRO-VACUUM DEVICES

### 2.6.1 Metals and alloys with defined coefficient of thermal expansion

Certain difference in coefficient of thermal expansion is important – however this difference needs to be defined only in narrow working temperature range (e.g.  $-40$  to  $+50$  °C): for precise mechanisms, pendulums etc. Higher temperature ranges are needed for thermal bimetals; **alloys for glass and ceramics seals** need to meet very strict requirements. The coefficient of thermal expansion needs to be defined up to temperature, where the glass becomes malleable enough to wet the metal, or up to temperature, where the solder melts. **Glass-to-metal seal** can be fabricated from listed metals – these are required to have very stable coefficient of thermal expansion.

These factors strongly correspond to the structure of alloy – alloys with the same composition can have different coefficient of thermal expansion values or **Curie temperature**. This problem is solved by measuring the these values and then choosing the one with appropriate values. **Low concentration of dissolved gasses** is also very important. Gas can form bubbles in the seal thus reducing its strength. Gasses are removed by melting in vacuum furnace or annealing in protective atmosphere.

Coefficient of thermal expansion for soft glasses is not higher than  $9 \cdot 10^{-6} \text{ K}^{-1}$ . The value for platinum is similar. Molybdenum and tungsten are used to fabricate seals with hard glasses.

The metal needs to be conveniently oxidized to form strong vacuum seal with the glass. Formerly, this problem was the most complication in vacuum electronic production. Nowadays, the heating by flame is replaced by heating in high-frequency furnaces – metals are oxidized beforehand and the seal is formed in protective atmosphere. Annealing of the metals and alloys for seals is of great importance. Inter-operation annealing is executed in wet hydrogen or on air. Desired oxide is thus formed, the metal surface is also decarbonized and the impurities are removed.

### 2.6.2 Glass-to-metal seal materials

Glass-to-metal seals need to be **vacuum proof, mechanically** and **thermally resistant**. Both materials must meet these requirements:

- Both metal and glass must have very similar value of the **coefficient of thermal expansion** at all operation temperatures; otherwise, the stresses at the interface can damage the vacuum seal. Seals are **adjusted** and **non-adjusted**. Materials with maximum difference of coefficient of thermal expansion about  $\pm 1 \cdot 10^{-6} \text{ K}^{-1}$  can be used for adjusted seals. The difference for non-adjusted seals can be higher.
- Oxide layer on the glass-metal interface must be thin, with good adherence to both metal and glass and must be also soluble in glass. Suitable are copper and chromium oxide.
- Seal metals must have good electric and thermal conductivity and also need to be degassed completely.

#### **Glass-to-metal seals examples:**

**Platinum and platinum wire** for soft glasses. Platinum wire has Fe-Ni core encased in platinum (light bulb and semiconductor diodes production).

**Molybdenum and tungsten as seal metals** for hard glasses, e.g. molybdenum foil sealed with quartz glass. Tungsten is fabricated only in form of wire and rods, but it has the lowest coefficient of thermal expansion of all metals. It is therefore suitable for highly thermally stressed products.

**Copper cover wire** for seals with soft glasses - especially lead glasses. The core is made of **Ni-Fe** alloy with 41 % to 43 % Ni. The cover is made of **copper** (25 % to 30 % of the wire weight). Available in oxidized state and the surface is covered by borax. The cover is fabricated by plating **copper** tube on core enclosed with brass foil and forging; alternatively, the **copper** can be deposited galvanically – the product is then thinned by drawing to achieve desired dimensions.

**Fe-Ni-Co alloys.** The Fe-Ni<sub>28</sub>-Co<sub>18</sub> alloys with the coefficient of thermal expansion tolerance of  $\pm 0,6 \cdot 10^{-6} \text{ K}^{-1}$  (similar to the coefficient of hard glasses) are the most important alloys of this group. Commonly known as **covar**. Unlike binary Fe-Ni alloys with similar thermal expansion, covar has higher Curie temperature (reaching glass transformation temperature), so it is suitable for concordant seals. Alloy Fe-Ni<sub>28</sub>-Co<sub>23</sub> has higher coefficient of thermal expansion and no changes occur in its structure during cooling. The coefficient value is similar to corundum ceramics.

**Fe-Ni-Cr alloys.** Chromium increases the heat resistance of Fe-Ni alloy, it has stable austenitic structure up to  $-80$  °C. Chromium concentration is 1 up to 6 %. These materials are formable; dense oxide layer, easily fusing with glass, is formed by annealing in wet hydrogen or protective atmosphere. Fe<sub>52</sub>-Ni<sub>42</sub>-Cr<sub>6</sub> alloy has similar

thermal expansion as glass for black-white and colored TV screens and is used for production of reinforcing pegs and anode outlets. Seal is produced after previous high-frequency heating without human interaction.

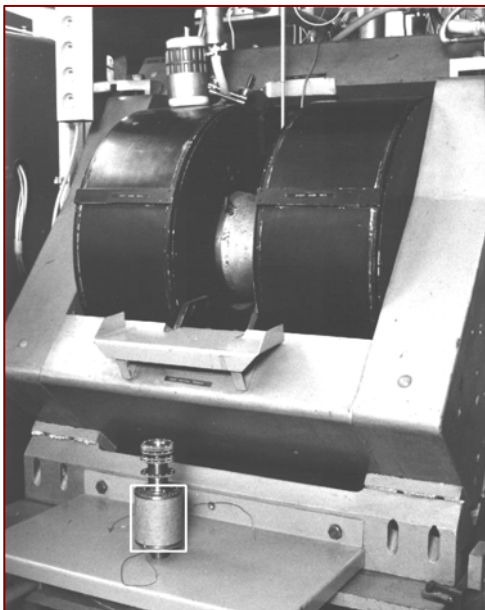
### **2.6.3 Metal materials for electro-vacuum devices**

Vacuum electrical engineering uses combination of plated metals to achieve desired properties. Low carbon steel, plated with aluminum from one side and with nickel from the other side, also called **PN**, is an example of such material. Fe-Al alloy changes color during heating, the surface blackens completely. Nickel coating keeps its gloss even at high temperatures. This material is thus suitable for receiving tubes anode production. The glossy layer faces the cathode to reflect the thermal radiation thus heating the cathode, the black is on the outer side and cools down the anode. Vacuum tube with such anode therefore has higher allowable throughput. Plating of the base material, usually steel, enhances its corrosion resistance (steel, single-side plated with copper) or improves its appearance (steel, both-side plated with nickel).

# 3. SUPERCONDUCTORS

Without a doubt, superconductivity is one of the most attractive topics in modern physics. Despite being discovered at the beginning of the twentieth century, it took many decades to put it in practice. What is **superconductivity** and how does it exhibit itself? Metal materials are usually good electric conductors. The fact, that passing current generates heat is also well-known. Amount of this heat rises with higher current densities and with specific electric resistivity of the conductor. Some alloys have high resistivity (e.g. canthal, nichrom etc.) and are therefore suitable for various heating devices, other conductors (e.g. copper, silver, gold, aluminum and others) have low specific el. resistance and are used for electricity distribution. Despite having low resistivity, one third of the transferred current is dissipated in form of heat. **Superconductor** with zero or close to zero resistivity would be thus very helpful.

Up to this date, superconductive materials start to exhibit these properties only at very low temperatures close to absolute zero (0 K). **Critical temperature**  $T_c$  is the temperature when material becomes superconductive. Resistivity of such material decreases as it is cooled, and, at critical temperature, its resistivity drops abruptly. The



material held under critical temperature is superconductive and does not oppose the passing current. It is thus possible to connect a coil from such material to and power source, let the current pass, and disconnect the source – the current in the coil flows without dissipation for very long time (several years). Current also produces magnetic field around the coil – **superconductive coil is a source of magnetic field**. This facilitates the **superconductive magnet** principle, employed whenever strong magnetic field is required and suitable coolant is available.

Essential advantage is that the diameter of the conductor can be, due to its zero resistance, significantly reduced – this allows for safe conduction of relatively high currents. Even small coils can have large number of threads.

**Fig. 3.1** Comparison of common electromagnet (large black coil on top) and superconductive magnet (bottom-left in white frame)

Intensity of magnetic field is proportional to the number of coil threads and passing current – very high number of coil threads in superconductive coil lowers the current necessary to generate magnetic field with similar intensity as in common magnet. Superconductive coil can therefore generate very strong magnetic field (several tesla units) with only tens of amperes – normal coil would require small power plant to achieve such intensity. Fig. 3.1 shows the difference in size of standard and super-conductive coil which would be required to generate magnetic field of similar intensity using 100 A current. Small superconductive magnet generates field with double the intensity.

However, this chapter starts with advantages of zero specific el. resistance, employed for energy distribution. This attribute is undoubtedly useful, however, the high cooling expenses of the superconductive wire limit its wider spread. The research of high-temperature superconductive materials is very promising. Classical **low-temperature** superconductors are pure metals and their alloys (superconductivity manifests at temperatures under 23 K – liquid helium with boiling point of 4.23 K is therefore needed), the **high-temperature** superconductors have, in average, critical temperatures of 90 K, some even 136 K, that is, over the boiling point of nitrogen (78 K). Liquid nitrogen is relatively affordable coolant. Common low-temperature metal-base superconductors have good formability and conductor fabrication is simple. High-temperature superconductors are generally very brittle ceramic materials and their fabrication is very demanding. Two separate ways, how to overcome brittleness of these materials, are nowadays studied – rolling of polycrystalline material in silver matrix (capillary) and welding or chemical deposition of crystalline superconductive layers on flexible, strip-shape, substrate. Modern technology allows production of superconductive strips up to roughly 1.5 km length.

## 3.1 EXAMPLES OF SUPERCONDUCTOR APPLICATIONS

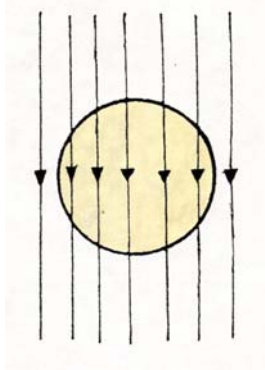
Superconductive magnets are nowadays employed in, for example, [elementary particle accelerators](#), in [material magnetic properties](#) research laboratories, also in medicine, e.g. [magnetic resonance tomography](#) - one of the least-harmful examination device. In industry, superconductors are utilized for [magnetic water purification](#) and other [magnetic separation processes](#).

**Superconductive magnets** (high-energy applications, magneto-hydrodynamic generators, plasma physics, thermonuclear reactions, etc.).

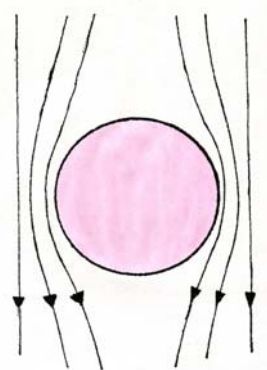
**Electric rotary machines** (homo-polar and hetero-polar machines, turbo alternators with superconductive coil wiring).

**Measuring equipment** (high-accuracy measurements, super-low intensity magnetic fields measurement).

**Superconductive levitation** utilizes electromagnetic induction and zero specific resistance of the superconductor. Material, placed in magnetic field, generates eddy current so the exterior magnetic field is kept outside the bulk material. Heat, generated by eddy current dissipation, increases with higher specific resistivity. After a while, all the eddy currents are consumed and heat dissipated and the magnetic field enters the material. Final stage of this phenomenon is shown on Fig. 3.2. Superconductor has zero resistivity, no current is therefore dissipated; if placed into magnetic field, the bulk of the superconductor material is completely shielded. The exterior magnetic field is thus deformed, as shown on Fig. 3.3.



**Fig. 3.2** Non-superconductive material placed in magnetic field. The field penetrates the material freely.



**Fig. 3.3** Superconductive material placed in magnetic fields keeps the bulk in its former state (zero magnetic field intensity), and the outer magnetic field is therefore pushed away.

What does this have to do with levitation? Let's look at another pair of figures. Superconductive material at temperature higher than critical temperature (therefore non-superconductive) placed in magnetic field generates shielding currents which are quickly dissipated by el. resistance and the field enters the material. If we cool the superconductive material below its critical temperature it becomes superconductive. Passing the critical temperature does not alter the magnetic field in the "superconductor", no current is generated and the magnetic field present in the material before cooling gets "frozen" inside the material in the same state as before cooling.

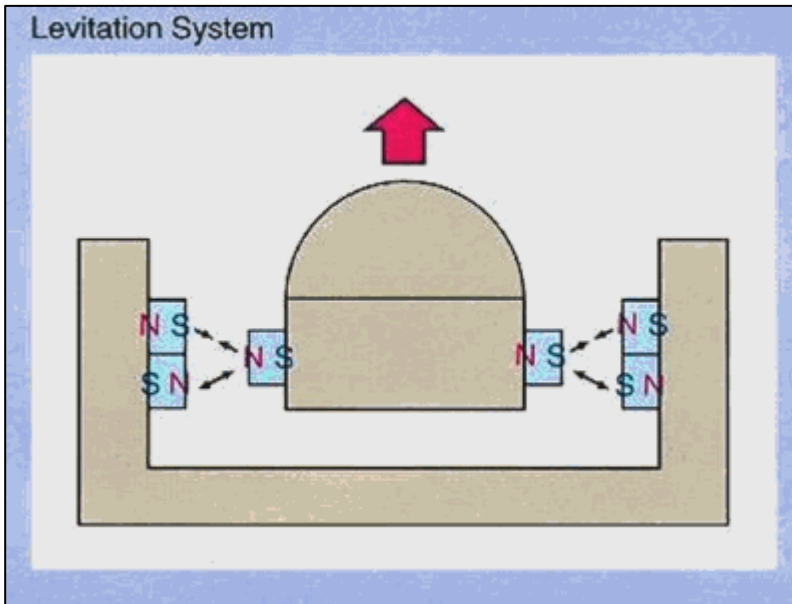
In fact, magnetic field does not flow directly through superconductive material but through microscopic non-superconductive channels. These channels are called **vortexes** or superconductor holes. Shielding currents flow through their perimeter, therefore shielding the surrounding superconductive material from magnetic field inside the vortex. Each vortex carries on or more elementary units, so called quanta of magnetic flow.

Any change of the exterior magnetic field (increase or decrease of intensity or even change in polarity or distribution) generates shielding current on the surface of the superconductor, compensating the change.

Consequently, if the permanent magnet is moved in any direction, the generated currents oppose the change, pushing the magnet back to its original location. It is thus held in a magnetic gap – it is hard to escape from this gap. This situation is a complete opposite to the situation with two permanent magnets. Not only can the magnet float above the superconductor, it can also hang under. This state is stable as long as is the superconductor cooled. Relative position of magnet and superconductor is stable to some degree – the magnet can even keep significant weight afloat together with it. Such device placed in vacuum (negligible air friction) with perfectly rotary symmetrical magnet (not just by dimensions but also the shape of the magnetic field), can operate as **lossless**

**bearing - flywheel.** Same principle is applied in **superconductive electric machine.** Flywheels of this kind are developed for satellite position stabilization. The temperature in space is favorably low so the cooling of the system is not a problem. Position stabilization is facilitated by forces generated during deviation of the flywheel axis from original. Flywheels of large scale and weight could be potentially used for energy storage – stored energy can be again converted to electricity and supply energy to, for example, space station.

**Magnetically levitated train**, also called **MagLev** (Fig. 3.5), has superconductor coils generating strong magnetic field on its sides (Fig. 3.4). This field generates current in copper coils in the sidetrack. Generated magnetic field interacts with the magnetic field of the copper coils in such manner, that it keeps the train afloat high enough above the track. Such train travels at speed of about 500 km per hour – the record is 563 km/h. Superconductive coils are fabricated from common superconductive materials, cooling is provided by liquid helium and its operation is therefore very costly. It is planned to replace the superconductive coils by permanent magnets made of superconductive material; lot of effort is being put into this matter.



**Fig. 3.4** Cross-section of the MagLev train and the U-track. Superconductive coils interacting with the track coils are depicted



**Fig. 3.5** MagLev on a test track in Yamanashi at about 200 km/h

Possible applications of superconductive materials are numerous – from super-fast switches (base component of future computers), [high-power transformers](#), [circuit breakers in power plants](#) or [gigantic ships with magneto-hydro-dynamic propulsion](#). Hundreds of other possible applications are being experimented with in laboratories, waiting for their chance.

## **3.2 THEORY OF SUPERCONDUCTIVITY**

Superconductive properties have been confirmed in many metals cooled under certain **critical temperature  $T_c$** . Some metal elements (e.g. As, Ba, Ge, Si, Se) also require high pressures to become superconductive, some lack it completely (Pt, Fe, Co, Ni, Ag, Cu, Au). Measurement of the magnetic field, generated by current in superconductive coil, intensity decrease revealed, that the material has specific resistance lower than  $10^{-25} \Omega \cdot \text{cm}$  (bellow critical temperature, i.e.  $10^{17}$  times lower than specific resistance of copper at 298 K).

Meisner and Ochsenfeld discovered that the superconductive material in superconductive state not only exhibits zero el. resistance, but also that **the bulk of the material cannot be penetrated by external magnetic field** (its intensity must be lower than critical intensity, material loses its superconductive properties otherwise). **The intensity of the magnetic field in the bulk of the superconductive material is zero.** However, the magnetic field penetrates thin surface layer called London penetration depth and it is about  $5 \cdot 10^{-6}$  cm for Pb, Sn, Hg and some other metals.

Fig. 3.6 shows the **relationship of electrical resistance on temperature** for classical low- and high-temperature superconductor. The resistance of superconductor decreases with decreasing temperature. The metals retain small, yet some resistance even at 0 K. After cooling bellow critical temperature ( $T_c$ ), the resistance in superconductor disappears - Fig. 3.6.

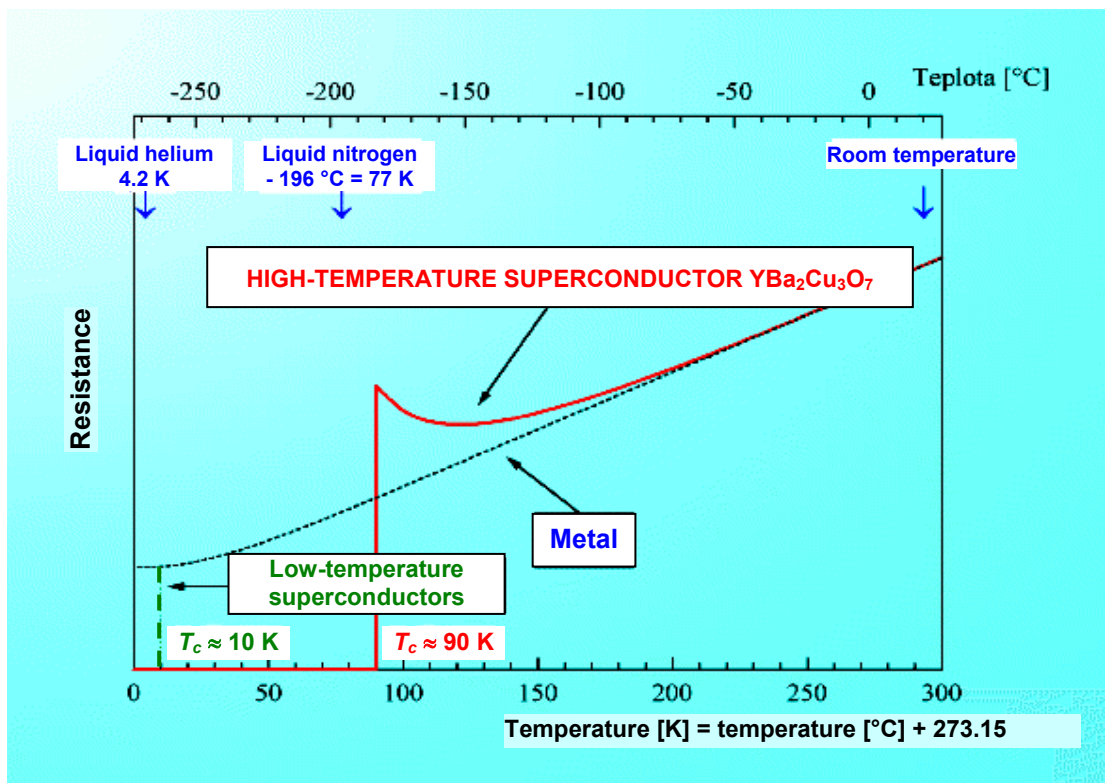


Fig. 3.6 Critical temperatures for low- and high-temperature superconductive materials

Superconductor placed in magnetic field with (intensity lower than critical) produces currents on its surface generating magnetic fields with opposite polarity and intensity (also below the critical level). Magnetic induction of superconductor is therefore zero – **superconductor is an ideal diamagnetic material**. This is utilized for shielding against external magnetic fields.

**Ideal conductor** – material with zero resistance.

**Superconductor** – **zero resistance** and **completely diamagnetic**.

It has been experimentally shown, that superconductivity can be canceled even by relatively small magnetic induction ( $10^{-3}$  to  $10^{-1}$  T). This, so called **critical limit of magnetic induction  $B_c$**  and it is temperature dependent.

**Outcomes of the superconductivity:** Total magnetic flowing through zero-resistance circuit is zero (unless the el. resistance changes).

Current flowing through the superconductor, generating magnetic field on its surface which exceeds the critical limit of magnetic induction  $B_c$  causes the material to lose its superconductive properties. Critical current  $I_c$  is affected not only by the type of the material but also by its shape. Superconductors with copper cover are used in applications, where current spikes can be expected - these can cause the transition from superconductive to normal state – copper can provide another current path for some time. This is especially important for high-temperature superconductors which are usually non-conductive in normal state.

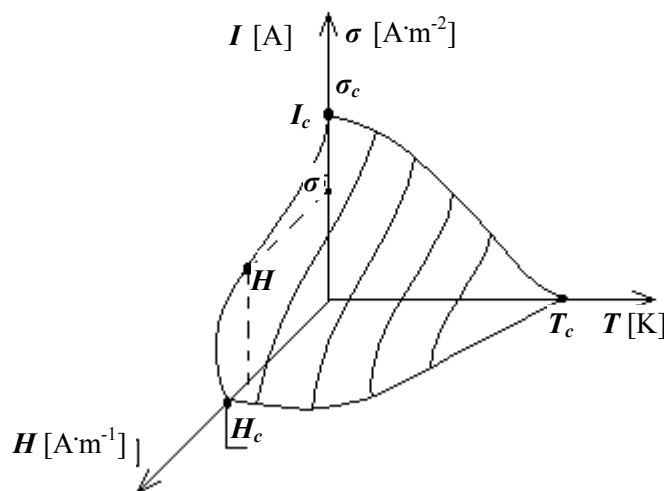
### Occurrence of superconductivity

**depends on :** **temperature  $T$ ,**  
**external magnetic field  $H$ ,**  
**transport current  $I$ .**

**Exceeding these so called critical limits** → superconductivity disappears (Fig. 3.7).

Superconductive ↔ normal transient by magnetic field is reversible.

Fig. 3.7 Relationship between superconductivity occurrence, temperature  $T$ , magnetic field intensity  $H$  and transport current  $I$





## Conductivity of low-temperature superconductors

Conductivity of low-temperature superconductors has been theoretically explained by Baarden, Cooper and Schrieffer. Basis of this theory lies in formation electron pairs with opposite spin by the exchange of phonons (phonon is defined as energy quantum of lattice vibration energy). This **electron-phonon-electron interaction** is stronger than repulsive electrostatic force between two same-polarity charges. This results in formation of **Cooper electron couple**. Superconductivity is however facilitated only by very small portion ( $\sim 10^{-4}$ ) of the total number of conductive electrons. Mean distance between the electrons couple corresponds to the coherent length  $D$  which is about  $10^{-6}$  to  $10^{-4}$  cm. Therefore, there are a large number of conductive electrons between any Cooper electron couple which are not part of any other couple. Wave functions of single couples overlap. Their movement through the lattice is loss-less.

That is why a system of accelerated electron in closed circuit keeps flowing; this **persistent current**  $\beta$  in **penetration depth**  $L$  and **coherent length**  $D$  is defined by equation:

$$\beta = L / D.$$

$\beta$  magnitude is temperature function; there are materials which can be, depending on the temperature (different temperature intervals) superconductors of different kinds.

### Superconductive range

Magnetic field penetrates only the thin surface layer of the superconductor – **depth of penetration**  $L$ .

Superconductive – normal borderline → continuous transient - **coherent length**  $D$ .

### Superconductor characterization:

a) **By the  $\beta$  parameter** two basic types are recognized:

Superconductors of the type I ...  $\beta < 0.7$  (e.g. for Pb:  $\beta = 0.4$ ).

Superconductors of the type II ...  $\beta > 0.7$  (e.g. for Nb<sub>3</sub>Sn:  $\beta \sim 50$ ).

**Type I superconductor** (**soft, ideal**) push away magnetic field.

Pure metals: Al ( $T_c = 1.2$  K), Sn ( $T_c = 3.37$  K), Pb ( $T_c = 7.22$  K), Hg ( $T_c = 4.15$  K).

**Type II superconductor** (**hard, non-ideal**)

Mostly *alloys + intermetallic compounds*, pure metals only rarely.

They are ideally pure **homogeneous** superconductors – only rarely conductive if the critical intensity of magnetic field is exceeded.

Non-homogeneous superconductors type II are reversible, critical intensity of magnetic field goes as high as  $8 \cdot 10^3$  kA·m<sup>-3</sup>.

**Hard superconductors** – superconductive properties disappear at magnetic field intensity around  $10^6$  A·m<sup>-1</sup>.

**Soft superconductors** – superconductivity disappears around  $10^3$  A·m<sup>-1</sup>.

Ferromagnetic materials (Fe, Ni, Co)

**not** superconductive – exhibit strong magnetisms.

Well-conductive materials (Cu, Ag, Au, Pt)

**not** superconductive.

b) **By the critical temperature**  $T_c$  [K]

**Low-temperature superconductive materials.**

**High-temperature superconductive materials.**

## 3.3 LOW-TEMPERATURE SUPERCONDUCTIVE MATERIALS

Almost all metals with superconductive properties belong to the type I semiconductor group, with the exception of Nb, Tc and V (some are listed in Table 3.1). Type II superconductors are the three metals mentioned above, and all alloys and all other superconductive compounds. Both types (I. and II) of superconductors are differentiated by their **behavior in external magnetic field** (Fig. 3.8).

**Type I** superconductor: transient to superconductive state by decreasing the intensity of magnetic field occurs **abruptly**. This means that at certain intensity this fields completely disappears in the bulk of the material and material becomes superconductive. This transient **is reversible**.

**Type II** superconductor is characteristic by **two limit values of critical intensity of external magnetic field**,  $Hk_1$  and  $Hk_2$ . In the range of  $H < Hk_1$ , the magnetic field does not penetrate the superconductor material – same as the type I superconductor. Increasing the intensity of magnetic field  $Hk_1 < H < Hk_2$  allows the external magnetic field to penetrate the material forming tubes of magnetic flow, **fluxoids**. Material inside these tubes is in normal state, the surrounding material is superconductive. Further increase of the intensity of external field increases the portion of the non-superconductive phase; superconductivity **disappears at  $Hk_2$  intensity**. This is, similarly to the type I semiconductor, reversible. Material in the  $Hk_1$  and  $Hk_2$  interval is called **mixed state superconductor**. Values of  $Hk_1$  are typically in the magnitude of  $10^4 \text{ A}\cdot\text{m}^{-1}$ , corresponding induction is about 1 T.  $Hk_2$  values are typically around  $10^7 \text{ A}\cdot\text{m}^{-1}$ , corresponding induction is about 10 T.

**Table 3.1** Transient temperatures and values of magnetic induction of chosen metallic superconductors

| Material     | Al*    | Pb*    | Ga*    | Mo*    | Nb     | V      | Nb <sub>3</sub> Sn | Nb <sub>3</sub> Ge |
|--------------|--------|--------|--------|--------|--------|--------|--------------------|--------------------|
| $T_c$ [K]    | 1.75   | 7.2    | 1.08   | 0.91   | 9.2    | 5.4    | 18.5               | 23,2               |
| $B_c(0)$ [T] | 0.0105 | 0.0803 | 0.0059 | 0.0096 | 0.2060 | 0.1408 | 22                 | 60                 |

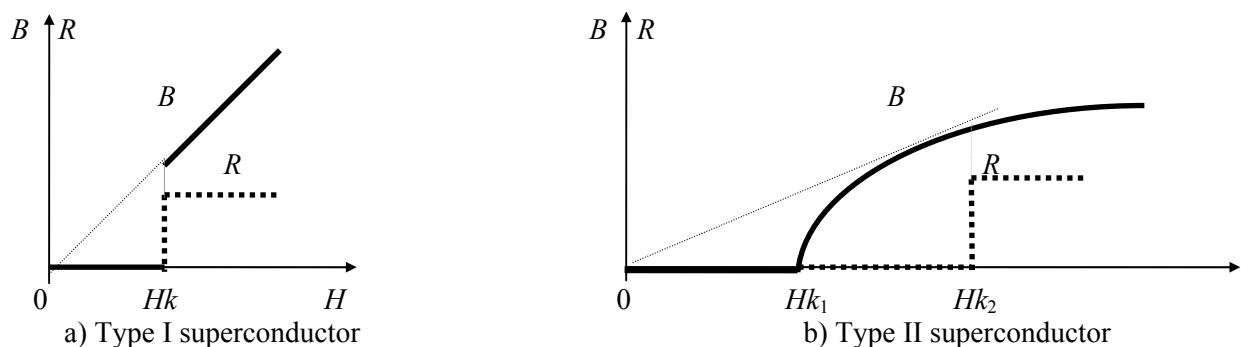
\* Type I superconductor, the rest is type II semiconductor

| Metal, alloy | $T_c$ [K] | Compound           | $T_c$ [K] | Compound           | $T_c$ [K] |
|--------------|-----------|--------------------|-----------|--------------------|-----------|
| V            | 5.1       | Nb <sub>3</sub> Sn | 18.5      | V <sub>3</sub> Ga  | 16.5      |
| Nb           | 9.2       | Nb <sub>3</sub> Ge | 23.2      | V <sub>3</sub> Si  | 17.1      |
| NbZr         | 10.8      | Nb <sub>3</sub> Al | 17.5      | Ti <sub>2</sub> Co | 3.44      |
| NbTi         | 9.5       | NbN                | 16.0      | La <sub>3</sub> In | 10.4      |

Current flowing through type II superconductor placed in magnetic field allows the fluxoids to move due to existence of Lorentz forces. However this generates heat and the critical values decrease. This can, in some cases, cause the transient to normal state. To prevent the migration of fluxoids in the superconductor material (homogeneous), lattice imperfections (foreign atoms, dislocations and others) are induced – these hinder the movement of fluxoids by binding them. Such superconductor is called **non-homogeneous type II superconductor** or **hard superconductor**. Magnetization curve of such material is no longer reversible and **hysteresis loop** is formed causing energy losses in alternating field.

The type II superconductors are utilized almost exclusively. So far, over a thousand superconductive compounds and alloys have been discovered. Superconductive materials can be also prepared from materials which are non-superconductive in their pure state. Nb-Ti, Nb-Zr and Nb-Ti-Zr alloys and Nb<sub>3</sub>Sn, V<sub>3</sub>Ga, Nb<sub>3</sub>Ge, Nb<sub>3</sub>Al and Nb<sub>3</sub>Al<sub>0.8</sub>Ge<sub>0.2</sub> compounds are the most-frequently utilized superconductive materials.

Behavior of type I superconductors in magnetic field is depicted on Fig. 3.8 a), type II on Fig. 3.8 b).



**Fig. 3.8** Dependence of magnetic induction  $B$  in superconductor and its electrical resistance  $R$  on intensity of external magnetic field  $H$  at  $T < T_c$

### Low-temperature superconductor fabrication technology

**Nb-Ti-Zr** alloys and intermetallic compound **Nb<sub>3</sub>Sn** have, so far, the widest variety of application.

**Nb-Ti-Zr** – solid solution => expected good formability => allows for wire fabrication.

**Fabrication technology** of superconductive materials is based on its character and properties. Nb-Zr, Nb-Ti and Nb-Ti-Zr alloys are typically manufactured by melting in vacuum electric arc furnaces. After casting, they are worked, typically by rolling, to produce desired semi-finished products – wires and rods. From these, various conductor types are produced by rolling the semi-finished product together with copper coating or by drawing. The conductors are produced as single-lined (diameter of Nb line is typically 0.2 mm, diameter of copper coating about

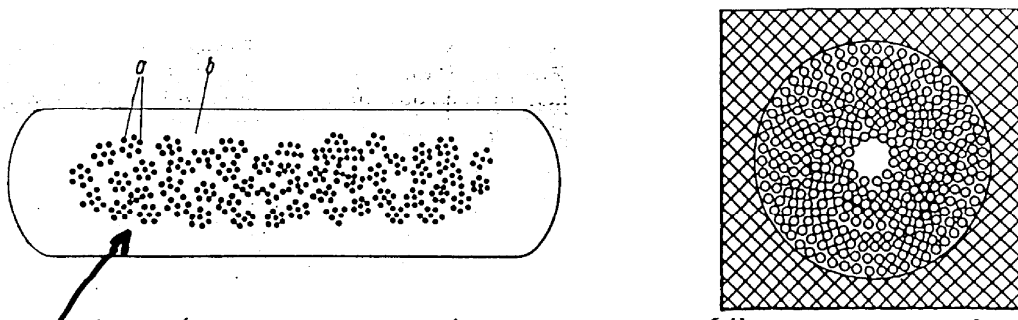
0.5 mm), multi-wire (tens of lines with diameter around 0.1 mm in single Cu cover) or multi-thread conductors, where, up to several tens of thousands of Nb-Ti threads (5 to 50  $\mu\text{m}$ ) are placed in single Cu or Cu-Ni matrix.

**Nb<sub>3</sub>Sn** – fabricated from Nb wires with deposited Sn layer + diffusive annealing => Nb<sub>3</sub>Sn. Nb<sub>3</sub>Sn is very brittle – sheaf of produced superconductor wires is incased in copper => such conductor is flexible and can be wired on a coil => the Cu layer can also serve as conductive surface in critical situations (local increase of temperature over  $T_c$ ). Applicable up to 15 T.

Two different kinds of fabrication are used for superconductive compounds production:

**Deposition technology** is based on reduction of elements from chloride vapor. Nb and Sn powders at 1000 °C react with HCl vapor to form NbCl<sub>5</sub> and SnCl<sub>2</sub>. These are, along with H<sub>2</sub> pumped into the reaction chamber – thin Cu (Nb or steel) wire or strip is continuously dragged through this chamber. Optimized technology can produce up to about 9 m of superconductive wire per hour. Nb<sub>3</sub>Ge wire is fabricated similarly.

**Diffusion technology** is facilitated by diffusion and concurrent reaction of components of A<sub>3</sub>B type compounds at higher temperature. Nb or V substrate, in form of wire or strip, is firstly covered with tin or gallium; the substrate is then heated. Diffusion of elements enables to form superconductive Nb<sub>3</sub>Sn or V<sub>3</sub>Ga. After this, the superconductor needs to be coated with stabilizing agent – usually copper. Strip superconductors, fabricated by one of the mentioned technologies, are suitable for magnet production and withstand currents up to 100 A at field intensity higher than 15 T.



a) Superconductive wire, b) Cu matrix. Cross section of superconductor with 102 Nb-Ti threads

**Fig. 3.9** Design of chosen superconductors

Other technologies of multithread conductor production are based on diffusion of tin from brass to niobium or through the copper cover.

#### **Application of low-temperature superconductors:**

- Loss-less electricity transport **by superconductive wires with their cover filled with liquid helium**
- High-power superconductive cables for loss-less energy transport
- Communication or control signal transfer in low-power electronics
- Superconductor magnets – generation of strong magnetic fields in large volumes
- Superconductor chambers for magnetic shielding
- Superconductor floating devices
- Superconductor cavity resonators
- Electric switches, rectifiers, logic circuits and memory chips
- Thermal switches, generators, detectors, microwave amplifiers
- High-sensitivity devices for measurements of magnetic field, current, voltage, temperature
- Medicine – brain neuron scanning, general examination, human fetus examination

**It is necessary to mention** that zero resistance providing loss-less current transport is of a great benefit, however, this is offset by the necessity of cooling by expensive liquid helium.

## **3.4 HIGH-TEMPERATURE SUPERCONDUCTORS**

Discovery of the ceramic superconductive materials based on copper, barium and yttrium oxides was a big achievement. Superconductive material, with critical temperature of the main component above 90 K, was therefore produced. This temperature is above threshold given by boiling point of nitrogen (77 K). Liquid nitrogen is about 30 times cheaper compared to the liquid helium. It is produced from air by liquefaction.

**Requirement of  $T_c \sim 2/3$**  for the cooling temperature  $\Rightarrow T_c > 105$  K.

Structure study of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  lattice revealed planes with chemically bonded  $\text{Cu}+\text{O}_2$ . The **oxygen content can be changed in wide interval** without changing lattice structure. **Rare earth elements and alkaline earth metals** form the basic structure supporting the strings of Cu and  $\text{O}_2$ .

### Physical properties of high-temperature superconductors

#### a. Critical temperature $T_c$

Real achievable temperature  $3/4 \div 2/3 T_c$ .

At  $3/4 T_c$ , the critical intensity of magnetic field  $H_c$  reaches about a half of low-temperature limit  $H_{c0}$  and critical current density  $I_c$  is about  $\sim 1/4$  of the limit value.

Example: with liquid nitrogen  $\text{N}_2$  (78 K) as and coolant, superconductive material with  $T_c \sim 100$  K can be used.

Material of  **$\text{YBa}_2\text{Cu}_3\text{O}_x$**  type (also called **YBCO** or „1-2-3“) with  $T_c = 95$  K represents borderline option.

(Material operated at 293 K would need to have the  $T_c$  about 400 K).

#### b. Upper limit of magnetic field intensity

$\text{YBa}_2\text{Cu}_3\text{O}_x$  (1-2-3) has extremely high value of limit field intensity. It depends on the relative orientation of the field and a, b, c axis of the orthorhombic lattice of the superconductor. Values are in range of 30 T (c axis) to about 200 T (a, b axis) at  $T = 4.2$  K.

#### c. Critical current density $\sigma_c$

Requirements:  $\sigma > 10^3 \text{ A}\cdot\text{mm}^{-2}$  for „volume“ conductors (power plant industry applications) and for thin superconductive foils.

$\text{YBa}_2\text{Cu}_3\text{O}_x$ :  $\sigma \sim 10^2 \text{ A}\cdot\text{mm}^{-2}$  at 4.2 K and magnetic field intensity of 6 T.

The  $\sigma_c$  decreases rapidly: at to 77 K and 6 T to  $1 \div 10 \text{ A}\cdot\text{mm}^{-2}$ . Reaching highest possible  $\sigma_c$  over  $T = 78$  K  $\Rightarrow$  basic requirement for practical application of volume high-temperature ceramic superconductors. Prerequisites for application:  $\sigma_c \sim 10^3 \text{ A}\cdot\text{mm}^{-2}$ ,  $T = 78$  K, magnetic field intensity 5 T.

Epitaxy-grown thin foils:  $\sigma_c \sim 10^4 \text{ A}\cdot\text{mm}^{-2}$ ,  $T = 78$  K at very low magnetic field intensity (meet the microelectronics requirements).

#### d. Chemical stability

1-2-3 type material is reactive at normal temperature. Humidity and  $\text{CO}_2$  cause deterioration  $\Rightarrow$  formation of hydroxides and carbonates. Prevention: protective coating! The coating prevents the diffusion in outer layers (especially in thin foils) – otherwise degradation of superconductive properties.

#### e. Radiation effect

High-temperature superconductive ceramic is more sensitive to radiation than conventional superconductors (potential problems with application in extremely strong magnets in fusion reactors).

#### f. Frequency effect

Conventional superconductive materials show some resistance in AC configuration; energy losses in oxide-based superconductors are expected to be smaller.

#### g. Material characteristics

High strength  $\Rightarrow$  danger of brittle fracture, suitable preparation methods  $\Rightarrow$  deformation before final oxidation  $\Rightarrow$  coil wiring.

High-temperature conductive materials known up to this date are basically **ceramic**. First was the  **$\text{LaBa}_2\text{Cu}_3\text{O}_{7-x}$**  compound. Shortly after that, more favorable physical properties have been discovered in the similar material with **lanthanum** replaced by yttrium ( **$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$** ). Best superconductive properties are reached with **x** close to 0.1. In this material, also called “1-2-3“, **yttrium** can be replaced by almost any rare earth elements or by **scandium**. Materials with yttrium replaced by cerium, praseodymium or terbium do not exhibit superconductive properties.

Structure of the ceramic superconductors of 1-2-3 group is orthorhombic similar to the structure of perovskite – difference is the oxygen deficiency. Structure with fully-occupied oxygen spots would have the  $\text{YBa}_2\text{Cu}_3\text{O}_9$  formula and the compounds would have layered structure of  $\text{BaCuO}_3:\text{CuO}:\text{BaCuO}_3$  type. Superconductive phase of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  formula is formed by heating the compound above  $500^\circ\text{C}$  – this forces the oxygen to escape the structure, and the structure (yttrium and barium ions separated by layers of copper and oxygen) develops oxygen vacancies.

Another type was compound with approximate formula of  $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_x$ , with  $x$  being about  $8 \div 9$ . The resistance decrease starts around 115 to 120 K; the resistance disappears completely at cca 90 K. This material seems to be most favorable of the above mentioned due to its time stability. Unlike type 1-2-3 which deteriorates over time in humid and  $\text{CO}_2$  containing environments, this material remains stable.

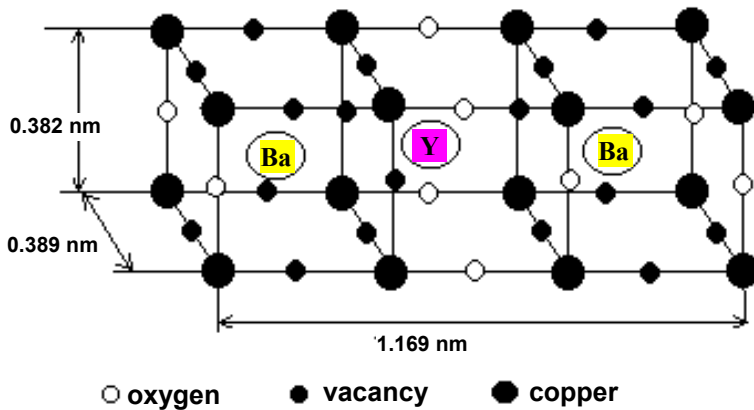


Fig. 3.10 Idealized elementary orthorhombic cell of  $\text{YBa}_2\text{Cu}_3\text{O}_7$

### Structure characteristics of the high-temperature ceramic superconductors

Oxygen – strong influence in the lattice of ceramic superconductors

- Orthorhombic phase structure can be described as „layers“ in the „c-axis“ plane constituted by layers of  $\text{CuO}$ ;  $\text{BaO}$ ;  $\text{CuO}_2$ ;  $\text{Y}$ ;  $\text{BaO}$ ;  $\text{CuO}_2$ ;  $\text{BaO}$  and  $\text{CuO}$ .

**Superconductive  $\text{YBa}_2\text{Cu}_3\text{O}_x$  material** is  $\text{O}_2$  sensitive

- Orthorhombic superconductive phase undergoes transformation at higher temperatures ( $\sim 700^\circ\text{C}$ ) to oxygen-deprived tetragonal phase,
- However, two different types of superconductivity exist in discussed crystal system – high-temperature ( $\sim 95\text{ K}$ ) and low-temperature ( $\sim 50 \div 60\text{ K}$ ) ~ depending on the  $\text{O}_2$  concentration,
- $\text{O}_2$  content drops quickly above  $550 \div 600^\circ\text{C}$ ,
- Orthorhombic phase  $\text{YBa}_2\text{Cu}_3\text{O}_x$  ( $x > 6.4$ );  $T < 750 \div 800^\circ\text{C}$ ,
- Tetragonal phase  $\text{YBa}_2\text{Cu}_3\text{O}_x$  ( $x < 6.4$ );  $T > 750 \div 800^\circ\text{C}$ .

There are three known effects of  $\text{O}_2$  based on its concentration:

1. Lattice parameter is practically constant if  $7.0 > x > 6.8$ ;
2. Changes in lattice parameters when the plateau of  $6.7 > x > 6.4$  is reached;
3. Severe changes in lattice parameters for  $x \ll 6.3$

These intervals correspond to phase equilibrium limits of the three phases: two orthorhombic and one tetragonal.

### High-temperature superconductive ceramic fabrication procedures

Several processes are available for fabrication (synthesis) of superconductive ceramic with  $T_c \sim 95\text{ K}$ :

1. Basic structure is formed at  $600 \div 700^\circ\text{C} \Rightarrow$  tetragonal structure deprived of  $\text{O}_2$ .
2. Annealing in oxidation atmosphere  $\Rightarrow$  additional  $\text{O}_2$  induced to the structure  $\Rightarrow$  conversion of formal tetragonal system to orthorhombic  $\Rightarrow$  prerequisite for high-temperature superconductivity in Y-Ba-Cu-O system.

Problems: - Anisotropy of thermal expansivity,

- Deformation caused by lattice transformation  $\Rightarrow$  micro-cracks initiation  $\Rightarrow$  micro-crack prevention (fine-grained structure after sintering, grain size under 1 micrometer).

#### „Filled profiles“

- Superconductive powder is placed in Ag tube.
- Tube is then formed by drawing or rolling.
- Tube protects the superconductive material from the environment; in the case of semiconductor malfunction can operate as el. conductor.
- Thermal treatment close to melting point,  $\sigma_c \sim 1.5 \cdot 10^4\text{ A}\cdot\text{cm}^{-2}$ , magnetic field up to 26 T.

### „Powder metallurgy“

1. Calcination of  $Y_2O_3$ ,  $BaCO_3$  and  $CuO$ .
2. Mixing of the mixture with organic compound (methanol, xylene) – filler and plastificator.
3. Extrusion pressing of wires, tubes ( $d \sim 10$  mm,  $l \sim 15$  m). Before sintering, this material is flexible and can be reeled; coated with thin insulating layer of  $Y_2BaCuO_5$  (produced by reaction of  $CO_2$  with YBCO), resistivity  $\sim 10^3 \Omega \cdot cm$ .
4. Sintering in  $O_2$  stream, pressure  $1.3 \cdot 10^3$  Pa, temperature  $890$  °C.

For practical application, not only the fabrication technology of compact large superconductors with desired physical properties ( $T_c$ ) but also the shaping technology (wires, thread, strips, layers) must be refined. Thin layer on a suitable substrate can be produced by several technologies - deposition from vapor, sputtering, epitaxy, magnetron or laser techniques. Current densities in thin layers go as high as  $10^5$  to  $10^6$  A·cm<sup>-2</sup>.

Mixing powder of barium hydroxide, concentrated solution of yttrium nitrates and copper at  $100$  °C and drying this solution at  $150$  °C for about 12 hours provides another fabrication option. Substance produced by either technology is heated at  $750$  to  $1000$  °C in air. After cooling, the mixture is milled and pressed in tablets. After this, it is again annealed in oxygen stream at  $900$  to  $970$  °C for about 10 hours. The tablets are thus sintered and ceramic mass is formed. It is cooled down very slowly to room temperature, the cooling rate cannot exceed  $100$  °C/h. Thus prepared material can be drilled, ground, cut, polished, etc.

In some cases, ceramic or oxide powder is mixed with organic bonding agent; the mixture is then formed by extrusion pressing (wire). At this stage, the wire can be further formed or machined. After reaching desired shape, the product is heated (organic compounds removal) and then sintered to produce the final superconductor.

Layered superconductors can withstand higher current densities. These are also more favorable than wire because the brittleness of the material is not of an issue. The layers can be either thick or thin. Elementary methods used for thin layers preparation are: high-frequency sputtering, deposition from vapor, laser ablation, epitaxy and so on. Single crystal substrates with lattice parameters close to the deposited compound are required to achieve crystal growth. Examples of such substrates: sapphire, GGG substrates (gallium-gadolinium garnet), NdGG (neodymium-gadolinium garnet),  $ZrO_2$  and others. Their price is usually very high.

# 4. MAGNETIC MATERIALS

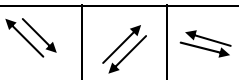
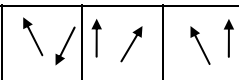
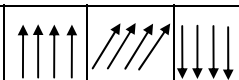
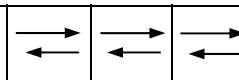
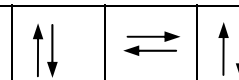
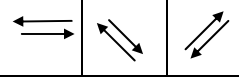
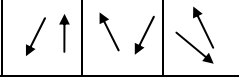
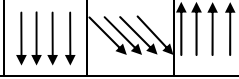
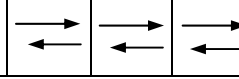
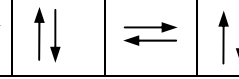
## 4.1 PHYSICAL PRINCIPLE OF MAGNETISM

Transport of particles with electric charge is always accompanied by generation of magnetic field in their vicinity. Particles with electric charge (electrons and protons) are moving constantly, so they create magnetic field in their vicinity. Existence of magnetic field (i.e. magnetism) is a natural property of substances.

Any particle with electric charge periodically moving in a circle (orbiting) is equivalent to electric circuit and creates **magnetic moment**. Magnetic moment is a vector. **Spin magnetic moment** of electron is of great importance for description of magnetic phenomena. Total magnetic moment of atom is derived from vector product of all electrons and protons; critical is the electron magnetic moment.

Based on magnitude of magnetic moment, we differentiate two groups: **diamagnetics** which have zero magnetic moment and **paramagnetics** with their atoms heaving magnetic moment. Some paramagnetics matters are able to, under certain circumstances, organize their atoms to separates domains with same magnetic moment orientation. Matters in this state are **ferromagnetic**. On the contrary, paramagnetic matters have antiparallel orientation of magnetic moments in the domains. Matter in this state is **antiferromagnetic**. Some antiferromagnetic matters consist of different atoms with different magnitudes of magnetic moment. The difference in the magnetic moments creates non-compensated magnetic moment in the domains. Such matters are called **ferrimagnetic**.

## 4.2 MAGNETIC MATERIAL - PROPERTIES

| Diamagnetism  | Paramagnetism  | Ferromagnetism  | Ferrimagnetism   | Antiferromagnetism  |
|---|--|---|--|---|
| Presumption:  |  |   |  |   |
| Atoms with full shells  | Atoms with incomplete shells   | Atoms with incomplete shells  | Atoms with incomplete (inner) shells with certain lattice structure                  | Atoms with incomplete shells, very low interatomic distance                           |
| Magnetic moment:  |  |   |  |   |
| No magnetic moment without external magnetic field. Compensation of spin moments    | Moment is ↓, exists without external magnetic field. Uneven distribution of moment vectors | Moment is ↑, spontaneous magnetization. Weiss domains, elementary magnets           | Moment exists due to incomplete compensation   | Moment compensation due to antiparallel alignment                                     |
| Direction of the moments:   |  |   |  |   |
|  |         |  |  |  |
|  |         |  |  |  |
| Permeability (susceptibility):  |  |   |  |   |
| $\mu_r < 1$ ( $\chi < 0$ )  | $\mu_r > 1$ ( $\chi > 0$ )   | $\mu_r \gg 1$ ( $\chi \gg 0$ )  | $\mu_r \gg 1$ ( $\chi \gg 0$ )   | $\mu_r \approx 1$   |
| Materials:  |  |   |  |   |
| Cu, Au, Ag  | Al, Sn, Pt   | Fe, Co, Ni  | Ferity   | MnO   |

Matters can be, based on the magnitude of relative permeability  $\mu_r$  and susceptibility  $\chi$  divided in four groups:

1.  $\mu_r < 1$  ;  $\chi < 0$  – diamagnetic materials
2.  $\mu_r = 1$  ;  $\chi = 0$  – magnetically neutral materials
3.  $\mu_r > 1$  ;  $\chi > 0$  – paramagnetic and antiferromagnetic materials
4.  $\mu_r \gg 1$  ;  $\chi \gg 0$  – ferromagnetic and ferrimagnetic materials

### 4.2.1 Diamagnetisms ( $\chi < 0$ ; $\mu_r < 1$ )

Not temperature or magnetic field intensity dependent  $\Rightarrow \chi = \text{const.}$

Superconductor  $\rightarrow$  extremely high susceptibility in superconductive state ( $\chi = -1$ )

No magnetic moment without external magnetic field, magnetization intensity has the opposite direction than the external magnetic field.

#### 4.2.2 Paramagnetism ( $\chi > 0$ ; $\mu_r > 1$ )

Matters with their own magnetic moment  $\Rightarrow$  result of uncompensated shell or spin magnetic moments:

zero magnetic field  $\rightarrow$  thermal oscillation  $\Rightarrow$  random magnetic moment orientation,

external magnetic field  $\Rightarrow$  moments turn in the direction of the magnetic field  $\Rightarrow$  matter exhibits certain level of magnetization. Magnetization has the same direction as the magnetic field.

#### 4.2.3 Ferromagnetism ( $\chi \gg 0$ ; $\mu_r \gg 1$ )

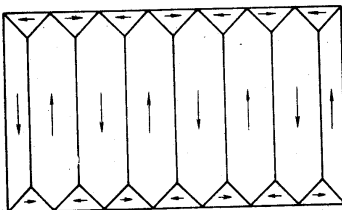
Ferromagnetic matters are characterized by:

- $\mu_r \sim 10^5$ .
- Incomplete outer electron orbitals 3d in Fe, Co, Ni, lanthanides have similar properties.
- Atoms of ferromagnetic materials can, under certain circumstances, become paramagnetic.
- Elementary magnets interact with each other  $\sim$  thermal oscillation  $\rightarrow$  **parallel configuration**.
- Strong magnetization in so called Weiss domains (**saturated magnetization**) even without external magnetic field.
- These domains are separated by so called **Bloch walls**, where the magnetic moment direction is altered.
- Crystalline lattice – regular distribution of atoms in crystal.
- Collectiveness of regular atom distribution in crystal lattice.
- Increasing the temperature above material specific, so called **Curie temperature**  $T_c$ , causes ferromagnetic material to become paramagnetic.

| Metal     | Fe   | Co   | Ni  | Gd  |
|-----------|------|------|-----|-----|
| $T_c$ [K] | 1043 | 1404 | 631 | 290 |

Existence of **ferromagnetic domains** with magnetic moments arranged parallel (due to the atomic interactions) under the Curie temperature is characteristic for ferromagnetic matters. Atoms need to be close enough to interact this way.

Heating of ferromagnetic matters causes inter-atomic distances to increase, number of atoms with parallel orientation of magnetic moments decreases; at **Curie temperature**, the domains vanish as well as the ferromagnetic properties. Despite existence of **domains** with magnetic moment, the ferromagnetic matters appear to have zero magnetic moment. Domains organize themselves to minimize the energy of the system. This configuration is depicted on Fig. 4.1; magnetic moments of four neighboring domains act as a separate magnetic circuit.

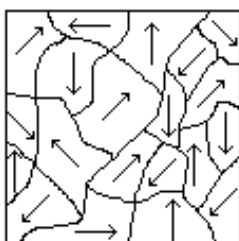


**Fig. 4.1** Minimum energy configuration of domains in ferromagnetic matter

Domain is a macroscopic structure, with length and width of several nanometers and about 0.001 to 0.1 mm thickness. Intensity of magnetic field inside the domains is very high – the domains are saturated. Neighboring domains are separated by layers called **Bloch walls**. Their thickness is usually around  $10^{-6}$  to  $10^{-4}$  cm, i.e.  $\sim$  500 to 5000 of inter-atomic distance units in crystal elemental cell. Domain structure can explain many important phenomena and properties of ferromagnetic materials, e.g. their magnetization in external magnetic field.

**Ferromagnetic domains** are dimensional structures grouping to form larger structures.

### Magnetization curve and hysteresis curve



Closely corresponds to the domain structure of ferromagnetic matters.

$$J = f(H), \quad J \text{ magnetic polarization [T], } H \text{ magnetic field intensity [A}\cdot\text{m}^{-1}]$$

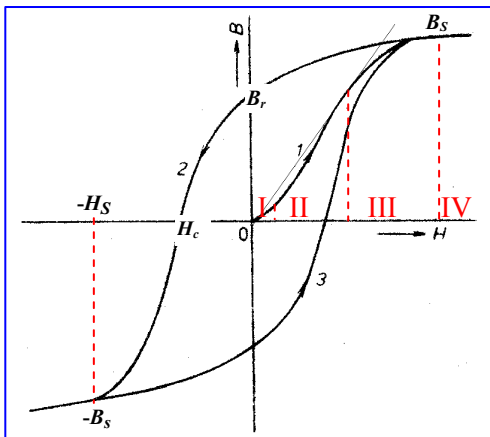
**Fig. 4.2** Characteristic of ferromagnetic matter (non-magnetized)

$\rightarrow$  domain distribution in ferromagnetics (no external field),  
 temperature below Curie temperature,  
 vector product of all magnetic moments is zero,  
 ferromagnetic is demagnetized, non-magnetic (virgin) state.



If we want to magnetize ferromagnetic matter which has not been magnetized after cooling below Curie temperature, we have to place it in an external magnetic field. Increasing the intensity of external magnetic field increases the magnetization of the material, and if sufficient intensity is reached, the material becomes magnetically saturated.

Magnetic induction – external magnetic field dependence curve has common shape, called **primary magnetization curve** – Fig. 4.3. This curve can be divided in four regions, based on the phenomena occurring in the ferromagnetic.



**Fig. 4.3** Hysteresis curve of ferromagnetic material

1 – primary magnetization curve, also called „virgin magnetization curve“,

2, 3 – curve segments corresponding to the opposite changes in magnetic field,

I – first region of magnetization curve (reversible shifts of walls),

II – irreversible turns (spontaneous magnetization in domains),

III – turning is finished,

IV – absolute value of magnetization slightly rises

Decreasing the intensity of external magnetic field of previously magnetized ferromagnetic matter results in lower values of magnetic induction compared to the first magnetization (Fig. 4.3). This phenomenon is called **magnetic hysteresis**. If the magnetic field is canceled, the induction does not drop to zero but remains at certain value of  $B_r$ , called **remanent magnetization** (or remanence). Magnetization gradually drops to zero if we magnetize the ferromagnetic in opposite direction. Magnetic field intensity which nulls the remanence is called **coercivity**,  $H_c$ . Increasing the opposite magnetic field intensity increases the magnetic induction up to saturated state. If decreased, the induction changes according to curve no. 3. Reversing the polarity of magnetic field again increases the intensity to value corresponding to saturated state. The magnetization cycle is hereby finished, its graphic representation is maximum **hysteresis curve**. Hysteresis also manifests during cyclic magnetization, if the intensity of altering magnetic field exceeds at least one region of irreversible shift of domain walls.

Ferromagnetic matters are, for example, metals ( $\alpha$  – Fe, Co, Ni, Gd, Tb, Dy, Ho, Er, Tm), their alloys, and also some compounds of ferromagnetic metals with rare-earth elements (particularly  $RCO_5$  compounds, where R can be Sm, Ce, Y, Pr etc.). Alloys comprising of non-ferromagnetic elements, such as Mn-Cu-Al alloys (Heusler alloys), also Mn-Ag-Al and others also can be ferromagnetic.

#### 4.2.4 Antiferromagnetism

Antiferromagnetic matters (antiferromagnetics) are solids with crystalline structure, magnetic domains are formed due to the interaction of their atoms. Magnetic moments of atoms in these are in **antiparallel configuration**. The opposite magnetic moments cancel each other; that is why antiferromagnetics have zero total magnetic moment up to the critical temperature (Néel temperature or Curie temperature), where the antiparallel configuration disappears. Above critical temperature, these materials behave the same as paramagnetics. Examples of antiferromagnetics are Mn and Cr, some oxides (e.g. MnO, FeO, NiO) and other compounds (MnSe,  $FeCl_2$ ,  $FeF_2$ ,  $CuCl_2$  etc.). Amorphous antiferromagnetics are also known.

#### 4.2.5 Ferrimagnetism

Is a special case of antiferromagnetism and occurs in crystalline matters. Ferrites are typical example.

**Ferrites** – iron oxide  $Fe_2O_3$  + oxides of other metals with oxidation state +2.

Sub-grid has different crystallography, with different type of ions which contain nodes.

The grids are not equivalent.

Spontaneous magnetization of sub-grid A is different than sub-grid B.

Magnetizations are not canceled by each other.

Ferrites exhibit some magnetic moment.

**Table 4.1** Some characteristics of cubic ferrites

| Ferrite type | Formula                                  | $J_S$ at 0 K [T] | $J_S$ at 20 °C [T] | $T_c$ [°C] | $\rho$ at 20 °C [ $\Omega \cdot \text{cm}$ ] |
|--------------|--|------------------|--------------------|------------|--|
| Mn ferrite   | $\text{MnO} \cdot \text{Fe}_2\text{O}_3$ | 0.70             | 0.50               | 300        | $10^6$                                       |
| Magnetite    | $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ | 0.64             | 0.60               | 585        | $4 \cdot 10^3$                               |
| Co ferrite   | $\text{CoO} \cdot \text{Fe}_2\text{O}_3$ | 0.60             | 0.53               | 520        | $10^7$                                       |
| Ni ferrite   | $\text{NiO} \cdot \text{Fe}_2\text{O}_3$ | 0.38             | 0.34               | 585        | $10^3 \dots 10^6$                            |
| Cu ferrite   | $\text{CuO} \cdot \text{Fe}_2\text{O}_3$ | 0.20             | 0.17               | 455        | $10^3$                                       |
| Mg ferrite   | $\text{MgO} \cdot \text{Fe}_2\text{O}_3$ | 0.18             | 0.15               | 440        | $10^3 \dots 10^6$                            |

$J_S$  – magnetic polarization at saturated state

## 4.3 FERROMAGNETIC MATERIALS

### Magnetization characteristics

Magnetic properties of ferromagnetic and ferrimagnetic materials in magnetic field are given by the relationship between **magnetic induction  $B$**  and **intensity of magnetic field  $H$** :

$$B = \mu H = \mu_r \mu_0 H$$

where  $\mu_0 = 4 \pi \cdot 10^{-7} \text{ H} \cdot \text{m}^{-1}$  is permeability of vacuum.

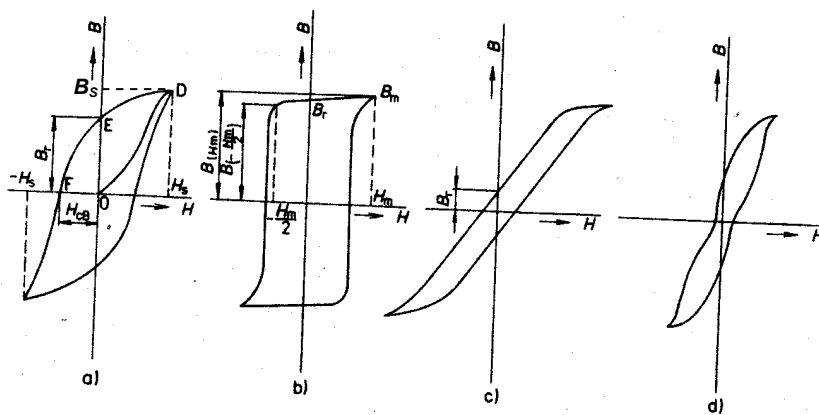
$B = f(H)$  function is not linear for ferromagnetic materials - their relative permeability  $\mu_r$  changes with magnitude of magnetic field intensity  $H$ , thus is usually described graphically.

Magnetization curve of material magnetized for the first time or after previous complete demagnetization is called **virgin magnetization curve** (Fig. 4.3). Along with hysteresis curve, it is one of the main characteristics of the magnetic material. Materials have different magnetization characteristics. These are acquired during direct current magnetization. Shape of these characteristics is different when alternating current is used.

**Magnetic susceptibility**  $\chi = \mu_r - 1$  is dimensionless and gives relative comparison between magnetic polarization and magnetic induction in vacuum.

### Shapes of hysteresis curve

Hysteresis curve of ferromagnetic material (Fig. 4.4) is closed magnetization curve, showing the  $B = f(H)$  during slow and steady change of magnetic field intensity from  $+H_S$  to  $-H_S$ . Magnetic field intensity  $H_S$  corresponds to the saturation point D. Hysteresis curve is gained by performing one cycle of magnetization. The OE section of hysteresis curve is called **remanence  $B_r$** , section OF **coercivity  $H_{cB}$** . Hysteresis curve starting from magnetic induction in saturated state  $B_S$  is called borderline (maximum) hysteresis loop.



**Fig. 4.4** Types of hysteresis curve  
a) normal type  
b) rectangular type  
c) flat type  
d) perminvar type

We differentiate several types of hysteresis curves based on their shape:

- a) normal – ratio of  $B_r/B_S = 0.5$  to  $0.8$  (Fig. 4.4 a)
- b) rectangular – ratio of  $B_r/B_S$  is close to one (Fig. 4.4 b)
- c) flat – ratio of  $B_r/B_S = 0.1$  to  $0.2$  (Fig. 4.4 c)
- d) perminvar – narrow part in the middle of the loop (Fig. 4.4 d).

Shape of the hysteresis loop is mostly affected by chemical composition and state of lattice which corresponds to the fabrication process, such as cold or hot rolling, annealing or quenching.

## Losses in magnetic circuit

**Hysteresis losses** correspond to the area of the hysteresis loop. Described by:

$$P_h \sim f B_{max}^{1.6} \quad f \text{ magnetization current frequency, } B_{max} \text{ maximum magnetic induction.}$$

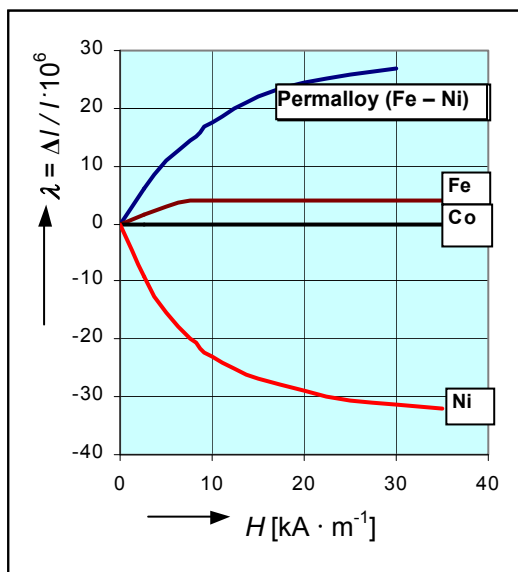
Change of the magnetic induction  $B$  in ferromagnetics results in generation of eddy currents. Current flowing through material dissipates as heat; eddy currents are thereby losing. Part of the energy put in the material during magnetization is transformed to heat (Joule heat). **Losses caused by eddy currents** correspond to maximum magnetic induction  $B_{max}$ , frequency  $f$ , material resistivity  $\rho$ , its thickness  $h$  and on construction adjustments of the material. These losses are described by:

$$P_v \sim f^2 B_{max}^2 h / \rho$$

To minimize the losses from eddy currents, material with high resistivity  $\rho$  and small thickness is used, for example: ferrites with up to  $10^5 \Omega \cdot m$ . Losses by eddy currents in transformers can be prevented by insulation between the sheets, alloying with low amount of silicon (reduces the resistivity to on sixth of the former value) or by lowering the induced voltage. Total losses in ferromagnetic materials are described by equation:

$$P_{Fe} = P_h P_v$$

## Magnetic anisotropy



Magnetic anisotropy in ferromagnetic materials causes the material to have different magnetic properties in different crystallographic planes. Magnetization is easier in one direction can be easier than in other. The direction of the easier and harder magnetization is described in relation to the crystal axis. Iron  $\alpha$  grain with BCC lattice is easier to magnetize along its (100) axis, slightly harder in the (110) direction. The least favorable direction for magnetization is (111). However in nickel (also BCC lattice), the (111) is the easiest magnetization direction.

## Magnetostriction

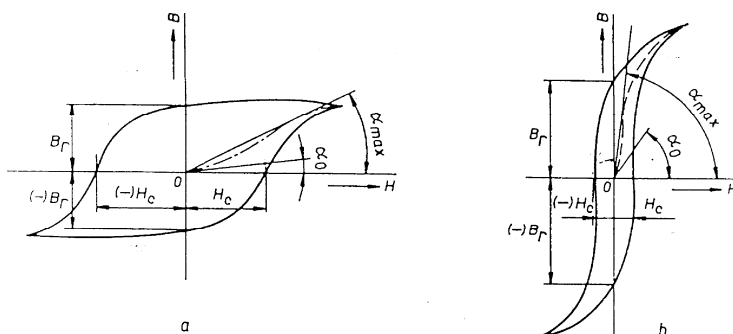
exhibits as changes in length and volume of ferromagnetic material by magnetic field. Its magnitude is described by magnetostriction coefficient  $\lambda$  which increases with magnetic field intensity and has its limit at saturation state – Fig. 4.5.

**Fig. 4.5** Magnetostriction in ferromagnetic materials in relevance to  $H$  magnitude  
 $\lambda$  – change in length (magnetostriction)

## 4.4 CLASSIFICATION OF MAGNETIC MATERIALS

Magnetic materials are, based on the requirements of electrical engineering industry, divided in several groups:

1. Magnetic soft materials (easy to magnetize and demagnetize, application in alternating magnetic fields),
2. Magnetic hard materials (difficult to magnetize and demagnetize, application in constant magnetic fields – permanent magnets),
3. Magnetic materials for special purposes.



**Fig. 4.6** Characteristic magnetic hysteresis curves:

- a) magnetic hard materials  
 $\uparrow H_c$ , virgin magnetization curve with small slope
- b) magnetic soft materials  
 $\downarrow H_c$ , step virgin magnetization curve

## 4.4.1 MAGNETIC SOFT MATERIALS

Characterized by their **narrow hysteresis loop**. Important properties are initial and maximum permeability ( $\mu_i$ ,  $\mu_{\max}$ ) maximum magnetic induction ( $B_{\max}$ ) which need to be as big as possible, low coercivity ( $H_c$ ). These materials are also required to meet specific requirements, such as high  $B_r/B_{\max}$  ratio for materials with rectangular hysteresis loop, magnetostriction properties ( $\lambda_{B_{\max}}$ ), high or low Curie temperature ( $T_c$ ), low or high thermal coefficient of induction, constant permeability, high electrical resistance, low thermal expansivity and so forth.

These materials are divided by their chemical composition in two groups: steels and Fe-Ni alloys. Appropriate crystallographic structure is achieved by combination of forming and annealing. The final annealing is essential if the top magnetic properties are to be achieved.

### Essential properties of magnetic soft materials:

- Easy to magnetize (even by weak magnetic field) and demagnetize.
- Narrow hysteresis loop.
- Low coercive intensity  $H_c$  ( $H_c < 800 \text{ A}\cdot\text{m}^{-1}$ ).
- High initial and maximum permeability.
- Low hysteresis and eddy current losses during magnetization.
- Usually low mechanical strength.

### Technical pure iron (Armco iron)

**Parameters:**  $\mu_i = 500$ ;  $\mu_{\max} = 15000$ ;  $H_c = 7.9$  to  $32 \text{ A}\cdot\text{m}^{-1}$

Highly pure Fe for non-alternating fields – low resistivity; alternating field  $\Rightarrow$  high eddy current losses.

**Fabricated** from iron pentacarbonyl:  $\text{Fe} + 5(\text{CO}) \rightarrow \text{Fe}(\text{CO})_5 \rightarrow \text{Fe} + 5(\text{CO})$  - high purity.

### Sheets and strips from electro-technical steel

Basic material for electro-technical sheets is iron with the highest saturation induction value ( $B_S = 2.15 \text{ T}$ ).

### Silicon steel

Silicon **decreases** hysteresis losses, (Fe + 0.5 – 4.5 % Si)

**Application:** rotary machines and transformer sheets for high voltage transformer stations.

Silicon steel is broadly used magnetic material in electrical engineering. Magnetic properties of strips produced from silicon electro-technical steel can be enhanced by grain crystallographic orientation, so called *texture*. This is achieved by combination of forming and rolling. Rolling direction is aligned with the easy magnetization vector. Electro-technical silicon steels are classified by the rolling technique and texture:

- \* **hot-rolled, isotropic**, silicon content (3.5 % to 4.6 %). Employed mainly in **media transformers** with guaranteed permeability at low magnetic field intensity and for **core of low-frequency chokes**.
- \* **cold-rolled, isotropic**, silicon content around 2.5 %. Mainly for **rotary machines**.
- \* **cold-rolled, anisotropic**, silicon content about 3 %. Produced in form of thin strips with directional structure. Often have insulation coating. Application: electromagnetic **immobile and rotary machines**, appliances.

**Application of sheets with directional structure** in transformers leads to reduction in size and weight, resp. increase in throughput compared to the sheets without directional structure. Transformer with the same throughput weighs about 25 % less, about 15 % less material for wiring is used. Special types of sheets with oriented structure for production of **small transformers, chokes, measurement, control and impulse transformers** are rolled to 0.05 mm thickness and width up to 100 mm, later cut into 10 to 30 mm strips. Used for production of ring (toroid) transformer cores or divided cores (by slicing the core).

**Insulation for the sheet surface** is very important. The surface of the hot-rolled sheets is oxidized – this is sufficient form of insulation for transformers operated up to 50 Hz. Larger transformers with operation frequency above 120 Hz require the sheets to be insulated from one side with sodium silicate or varnish. Cold-rolled strips must be insulated, since their surface is smooth and metal-glossy. For small motors and transformers operated up to 50 Hz, the oxide layer is produced during annealing in continuous furnaces at 550 to 800 °C.

### Alloys with high initial permeability (Ni-Fe alloys)

**Ni** – lowest anisotropy of all ferromagnetic materials, unfortunately also lowest magnetic polarization in saturated state (drawback). Ni forms substitution solid solution with Fe -  $\gamma$  phase (austenite) with FCC lattice, stable up to 67 wt. % Fe. Over 67 % of Fe  $\Rightarrow$   $\alpha$  phase with BCC lattice.

Curie temperature:  $\text{Ni} \approx T_c = 354 \text{ }^\circ\text{C}$   $\text{Ni} + 35 \text{ \% Fe} \approx T_c = 612 \text{ }^\circ\text{C}$

## PERMALLOY (35 to 80% Ni)

- Very good magnetic properties.
- After pure Fe, the second “softest” magnetic material.
- High  $\uparrow \mu_i$ ,  $\downarrow H_c$ ,  $\downarrow$  hysteresis losses.
- Max. permeability  $\mu_{\max} = 80\,000 \div 100\,000$ .
- Resistivity of permalloy is double the resistivity of pure Fe.
- Adjustment of properties by composition and thermal treatment.

### **Application:**

- Communications, electricity of various frequencies distribution.
- Transformer cores, chokes, magnetic shielding covers.

**Table 4.2** Magnetic properties of chosen Fe–Ni alloys

| Alloy                                       | $\mu_i$        | $\mu_{\max}$     | $J_S$ [T] | $H_c$ [ $A \cdot m^{-1}$ ] | $\rho \cdot 10^8$ [ $\Omega \cdot m$ ] |
|---|----------------|------------------|-----------|----------------------------|--|
| Supermalloy (78 % Ni + 5 % Mo + 17 % Fe)    | $1 \cdot 10^5$ | $1 \cdot 10^6$   | 0.80      | 0.3                        | 60                                     |
| 79 Permalloy (78 % Ni + 4 % Mo + Fe)        | $2 \cdot 10^4$ | $2 \cdot 10^5$   | 0.85      | 4                          | 55                                     |
| MU-metal (78 % Ni + 5 % Cu + Fe)            | $3 \cdot 10^4$ | $1 \cdot 10^5$   | 0.80      | 4                          | 42                                     |
| Hypernic (50 % Ni + Cu, Mn, Si, W, Co + Fe) | 4500           | $1 \cdot 10^5$   | 1.60      | 20                         | 45                                     |
| 45 Permalloy                                | 2700           | $2.3 \cdot 10^4$ | 1.60      | 24                         | 40                                     |

## Ni-Fe alloys with 75 to 80 % of nickel and other alloying elements

**Known for their highest values of initial and maximum permeability ( $\mu_i, \mu_{\max}$ ).**

These alloys have low coercivity and low hysteresis losses. Maximal induction is about 0.9 T. They are alloyed with other elements (Cu, Cr, Mo, Mn) and generally called „permalloys“. Excellent permeability is achieved by very precise magnetic annealing. This allows changing its hysteresis curve to the rectangular type.

## Ni-Fe alloys with 50 % of nickel

Highest magnetic induction of all binary alloys (1.55 T). Precise technology and selection of raw materials allows production of alloys with the same composition but dissimilar properties. Most importantly, the initial and maximum permeability can be increased up to  $\mu_i = 1000$ ,  $\mu_{\max} > 100000$ . Hysteresis curve can be modified to the rectangular type.

**Table 4.3** Properties of Ni-Fe50 alloy Nifemax, produced by VEB Auerhammer

| Alloy       | $\mu_i$ | $\mu_{\max}$ | Coercivity<br>$H_c$ [ $A \cdot m^{-1}$ ] | Magn. induction<br>$B_{\max}$ [T] | Resistivity<br>$\rho$ [ $\Omega \cdot m$ ] | Curie temperature<br>$T_c$ [ $^{\circ}C$ ] |
|-------------|---------|--------------|--|-----------------------------------|--|--|
| Nifemax 2.5 | 2500    | 25000        | 20                                       | 1.5                               | $450 \cdot 10^{-9}$                        | 470  |
| Nifemax 4   | 4000    | 30000        | 12                                       | 1.5                               | $450 \cdot 10^{-9}$                        | 470  |
| Nifemax 10  | 10000   | 50000        | 5  | 1.5                               | $450 \cdot 10^{-9}$                        | 470  |
| Nifemax 40  | 40000   | 80000        | 2  | 1.5                               | $450 \cdot 10^{-9}$                        | 450  |

## Ni-Fe alloys with 36 % of nickel

This alloy is generally called **invar**. Exhibits the lowest coefficient of thermal expansion of all magnetic alloys  $1.5 \cdot 10^{-6} K^{-1}$  at 0 to 100  $^{\circ}C$  and highest resistivity of  $850 \cdot 10^{-9} \Omega \cdot m$ . Its magnetic permeability and coercivity is comparable to fine silicon steels. Initial permeability of 2000 to 3000, maximal magnetic induction is about 1.3 T. Exhibits slow increase of permeability at low magnetic field intensity.

## Ni-Fe alloys with 30 % of nickel

Typically have low Curie temperature (30 to 100  $^{\circ}C$ ). This corresponds to strong correlation of temperature and maximum magnetic induction. Curie temperature can be adjusted by changing nickel content.

## Alloys with constant initial permeability in weak magnetic field

It is viable to use magnetic field during cooling (below Curie temperature) to achieve rectangular hysteresis loop. **Thermo-magnetic treatment** results in alignment of elementary areas during recrystallization. 65 % Ni

alloys (e.g. Dynamax) with desired structure can be produced by this technology. Steep hysteresis loop can be achieved also for 78 % Ni alloys by combination of cold rolling and annealing of very thin samples. A strip with the easy magnetization vector perpendicular to the strip length can be fabricated from alloys with 50 % Ni by suitable thermo-magnetic treatment – such material is called **Izoperm** and it has narrow loop with constant slope.

**Fe-Co** alloys have the highest saturation induction values. Alloy with 35 % of Co has the highest value of  $B_S$ .  $B_S = 2.43$  T. **Perminvar** has similar properties as Izoperm. **Permendur** (49 % Fe, 49 % Co, 2 % V) has rectangular loop with  $B_S = 2.15$  T.

**Perminvar:** 45 % Ni, 30 % Fe, 25 % Co, high resistivity,  $\mu_i = 450$  in constant magnetic field up to  $159 \text{ A} \cdot \text{m}^{-1}$ ,

**Izoperm:** 40 ÷ 50 % Ni, 3 ÷ 4 % Al, 10 ÷ 15 % Cu + Fe (balance),  $\mu_i = (30 \div 80)$  constant for magnetic field up to  $7.95 \text{ kA} \cdot \text{m}^{-1}$ .

### Alloys with temperature controlled permeability

Small change of temperature  $T \Rightarrow$  change of magnetic induction.

- **Termoperm** (Fe + 30 % Ni),
- **Calmalloy** (Ni + 30 ÷ 55 % Cu, 1 ÷ 2 % Fe).

### Fe-Co alloys

These alloys exhibit the highest magnetic induction. Fe – Co 35 % has  $B_{\max} = 2.4$  T, Fe – 50 % Co – 2 % V has  $B_{\max} = 2.35$  T and can be hot-rolled to thin sheet. This alloy has high magnetostriction at  $B_{\max}$  ( $\lambda_{\max} = 80 \cdot 10^{-6}$ ).

## 4.4.2 MAGNETIC METALLIC GLASS

**Amorphous magnetic materials** are also referred to as **magnetic metallic glasses**. They belong to the group of soft magnet materials. **Metallic glass** are not crystalline as common metallic materials, however they preserve the metallic appearance and have characteristic physical, mechanical and chemical properties which surpass the properties of crystalline materials of similar composition. These materials are homogeneous, movement of Bloch walls is effortless – this is why they are much magnetically softer compared to the similar crystalline material.

Some **properties of metallic glass** (e.g. specific density, compressibility) are identical to crystalline material. Metallic glass is not anisotropic, it has high **radiation damage resistance**. No noticeable structural changes have been detected in metallic glass even after strong irradiation.

**Mechanical properties:** very high yield strength, surpassing all metals, however some steels have similarly high fracture toughness. High yield strength is, from the physical point of view, caused by very low mobility of dislocations. This is due to the disorganization of the base structure and absence of slip planes. Metallic glass is prone to **plastic deformation** when strained due to its instability; however it can withstand **severe plastic deformation** when bent, sheared or pressed.

**Corrosion properties:** surface of the metallic glass develops homogeneous protective oxide layer, resistant to corrosion, especially in chlorides. Cr supports the formation of protective film.

**Magnetic properties of metallic glass:** Fe based metallic glass can be **magnetized easily**, especially compared to the Permalloy. Easy magnetization of metallic glass is related to the **high mobility of magnetic domain walls** in the matrix. The eddy currents are, thanks to its high el. resistance, hindered. High mobility also corresponds to excellent macroscopic magnetic properties. This, consequently, explains low specific watt losses (W/kg). Metallic glass is utilized in, for example, production of **transformers, amplifiers, switches, recording heads** etc.

**Table 4.4** Comparison of values for two transformer types (15 kVA)

| Parameter        | Silicon steel | Metallic glass |
|------------------|---------------|----------------|
| Current          | 2.5 A         | 0.12 A         |
| Watt losses      | 112 W         | 14 W           |
| Losses in copper | 210 W         | 166 W          |
| Total loss       | 322 W         | 180 W          |
| Energy savings   | 0             | 1250 kWh/year  |
| Temperature      | 100 °C        | 70 °C          |

**Advantageous and characteristic properties of amorphous metal** compared to ordinary metal:

- High hardness.
- Higher strength/weight ratio.
- Higher ultimate tensile strength and yield strength.
- High corrosion resistance.
- High resistivity.
- Unique sonic properties.

Fabrication methods of metallic glass are based on fast cooling – **rapid solidification** is necessary to achieve the amorphous structure. Base **requirements** for application of rapid solidification are:

- a) broad solid solution existence limit,
- b) refinement of precipitates (replaced by very fine precipitates),
- c) metastable crystalline phases (diffusion processes are hindered during rapid solidification),
- d) at certain cooling rate, the material cannot reach the crystalline structure and the liquid structure is attained, – metallic glass (amorphous, microcrystalline metals).

**Fabrication:** Rapid cooling of liquid metal

(RSP – Rapid Solidification Processing)

(RST – Rapid Solidification Technology)

Cooling rate – RSP  $\Rightarrow 10^4$  to  $10^6$  K·s<sup>-1</sup>; conventional rates  $10^3$  to  $10^0$  K·s<sup>-1</sup>

- ❖ Technology of very thin strips production facilitated by liquid metal being driven to fast rotating, cooled copper drum. Radial speed of the drum  $\sim 100$  km/h  $\Rightarrow$  strip up to  $80 \mu\text{m}$  thickness, 1 to 150 mm width.
- ❖ „Atomization” by spraying the liquid into fast stream of inert gas („jet” technology). Produces fast very fine solidified particles.
- ❖ Melt spinning – spraying of the liquid metal on rotating disc producing very fine particles.
- ❖ Cooling of very thin surface layer heated by laser.

**Table 4.5** Critical cooling rates  $v_c$  of some materials to produce amorphous structure

| Material         | $v_c$ [K·s <sup>-1</sup> ] | Material  | $v_c$ [K·s <sup>-1</sup> ] | Material                      | $v_c$ [K·s <sup>-1</sup> ] |
|------------------|----------------------------|---|----------------------------|-------------------------------|----------------------------|
| H <sub>2</sub> O | $10^{12}$                  | Fe <sub>80</sub> B <sub>20</sub>                  | $10^6$                     | SiO <sub>2</sub>              | $10^{-1}$                  |
| NaCl             | $10^{10}$                  | Fe <sub>80</sub> P <sub>13</sub> C <sub>7</sub>   | $10^4$                     | P <sub>2</sub> O <sub>5</sub> | $10^{-23}$                 |
| Ni               | $10^{10}$                  | Pd <sub>78</sub> Cu <sub>6</sub> Si <sub>16</sub> | $10^1$                     | Glycerine                     | $10^{-40}$                 |

**Metallic glass** is **perspective soft magnetic material**. Stream of liquid metal is jetted on fast rotating, intensively cooled drum – the metal is thus prevented from forming crystalline structure. Produced strip has about 10 to 50  $\mu\text{m}$  thickness and width in the magnitude of tens to hundreds of mm. It can be bend, formed, rolled and cut. Disadvantage of metal glass is its thermal instability. Heating above certain temperature starts the crystallization process; the favorable properties disappear. This temperature depends on the alloy composition and usually does not exceed 300 °C.

The „glass-state” can also be reached in alloys that can be super-cooled in liquid state.

Alloy types: **Fe, Co, Ni +10 ÷ 30 % (B, C, P, Si, ...)**. General formula of magnetic glass (Fe,Co,Ni)<sub>80</sub> (B,C,P,Si)<sub>20</sub>.

**Table 4.6** Properties of some metallic glasses

| Composition  | $B_S$ [T] | $H_c$ [A·m <sup>-1</sup> ] | $\mu_{\text{max}}$ |
|--|-----------|----------------------------|--------------------|
| Fe <sub>80</sub> B <sub>20</sub>                                 | 1.8       | 6.4                        | $1 \cdot 10^5$     |
| Fe <sub>40</sub> Ni <sub>40</sub> P <sub>14</sub> B <sub>6</sub> | 0.5       | 0.8                        | $4 \cdot 10^5$     |
| Co <sub>74</sub> Fe <sub>6</sub> B <sub>20</sub>                 | 1.2       | 3.0                        | $3 \cdot 10^5$     |

Chemical composition  $\Rightarrow \mu, H_c$ , shape magnetostriction. These materials exhibit several-magnitudes higher resistivity.

Fe<sub>86</sub>B<sub>7</sub>C<sub>7</sub> – magnetic polarization in saturated state  $J_S = 1.77$  T;  $\rho \sim 3$  times higher than Fe-Si alloy.

Co<sub>58</sub>Ni<sub>10</sub>Fe<sub>5</sub>B<sub>10</sub>Si<sub>11</sub>  $\sim H_c = 0.4$  to  $0.5$  A·m<sup>-1</sup>.

**Metal glass** has, compared to the electrotechnic steel, about five times lower losses from eddy currents.

### Application:

**Recorder heads:** ( $\uparrow \mu$ ,  $\downarrow H_c$ ,  $\downarrow$  anisotropy,  $\downarrow$  magnetostriction,  $\uparrow \rho \Rightarrow$  suppression of troublesome effects of eddy currents,  $\uparrow$  hardness  $\Rightarrow \downarrow$  abrasion,  $\uparrow$  lifetime).

**Transformer production**  $\uparrow \rho$ ,  $\downarrow$  thickness,  $\Rightarrow \downarrow$  hysteresis losses,  $\downarrow$  eddy-current losses.

$\Rightarrow$  total losses **5 times lower** than at classic magnetic soft materials!

Drawbacks: longevity and thermal stability, transformation to crystalline form.

**Transformer core construction**, production of high-quality low-cost **recorder heads for tape recorders, miniature microphones, magnetic amplifiers** and others.

**Magnetic shielding** – narrow strips threaded into wider strips, then layered with epoxide.

## 4.4.3 HARD MAGNETIC MATERIALS

Hard magnetic materials are utilized in technical practice for production of **permanent magnets** which generate magnetic field without current (unlike electromagnets). Physical basis of these properties are usually imperfections in the structure, hampering the reversion of magnetization. Other option is to use single-domain particles; their spontaneous magnetization and thus magnetic moment can be changed only with very strong external magnetic field. **High values of coercive intensity  $H_c$ , remanence  $B_r$  and maximum energetic product  $(BH)_{\max}$**  are required. Those are met by, for example **steel with high internal stress**. This explains the use of martensitic steel for quenched magnets – however, their structure is not stable and the material loses its magnetic properties over time. Other viable materials are hardenable non-formable alloys, hardenable formable alloys, powder materials, ferrites and also cobalt-rare earth elements compounds.

### Hysteresis loop

The shape of  $J(H)$ , resp.  $B(H)$  curve in Fig. 4.7 is characteristic for hard magnetic material. The shape of curve from  $+H_{\max}$  to  $-H_{\max}$  and back defines the **hysteresis loop**. It corresponds to the distribution of magnetic domains (Weiss domains) in the material. Two phenomena are distinguished: transport of domain walls and rotation of magnetization vectors. The first phenomenon takes place in lower-intensity fields, the other in the saturated state region. Fig. 4.7 depicts the differences of the two hysteresis loop types – the difference is provided by the additive component  $\mu_0 H$ .  $B(H)$  relationship is more common in technical use.

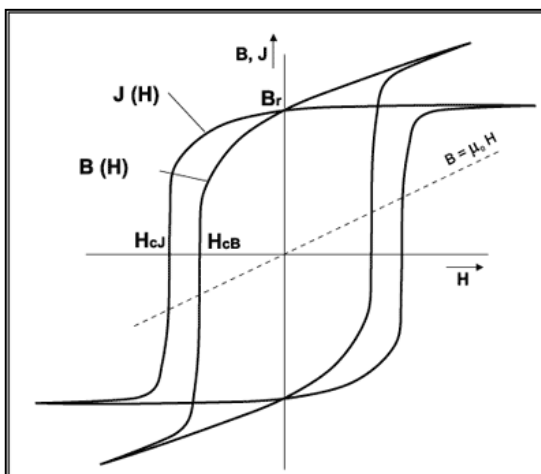


Fig. 4.7  $J(H)$  and  $B(H)$  relationship for hard magnetic material

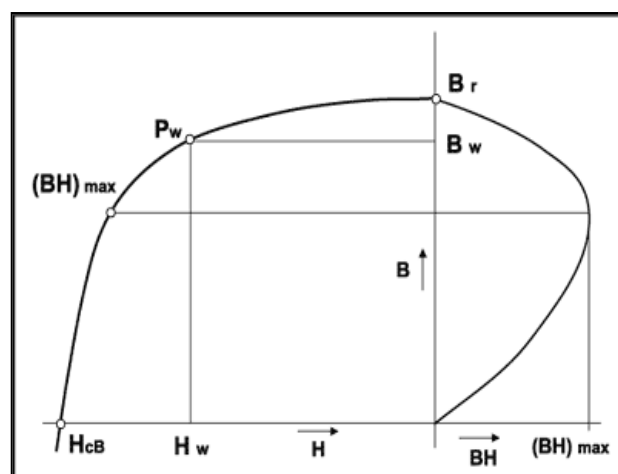


Fig. 4.8 Demagnetization curve of a magnet

### Characteristic values for permanent magnets

Permanent magnet is typically characterized by these basic parameters: coercivity  $H_c$  remanence  $B_r$  and maximum energetic product of  $(BH)_{\max}$ . Coercivity  $H_c$  [A/m] is the intensity of external magnetic field (opposite to the spontaneous magnetization) rendering the whole material non-magnetic,  $B = 0$ .  $H_c$  parameter is relative resistance against de-magnetization (by external or internal source). Remanence  $B_r$  [T] is magnetic induction remaining in the material in closed system after the magnetic field is removed. Fig. 4.7 shows that while  $B_r$  is identical for both types of the  $B(H)$  curve, the  $H_c$  parameter is different. Therefore, coercivity  $H_{cJ}$  and  $H_{cB}$  is recognized. The  $(BH)_{\max}$  [ $\text{kJ}\cdot\text{m}^{-3}$ ] (often called **maximum energetic product**) corresponds to the energy stored in



magnet of optimal shape. Parameter  $(BH)_{\max}$  corresponds to the interaction strength between the magnet and other ferromagnetic components (typically iron).

## Demagnetization

Demagnetization is decrease of total magnetic polarization of magnet. This can be achieved by external source of magnetic field of opposite polarity. This process is called demagnetization.

## Working point

Instead of the whole hysteresis loop, just the second quadrant (**demagnetization curve** - Fig. 4.8) is displayed; this part depicts the operation region of the permanent magnet and characteristic points. Working point  $P_w$  of permanent magnet is characterized by  $B_w$ ,  $H_w$  values. After demagnetization, this point shifts from remanence to the left along the magnetization curve to final  $P_w$ . In optimal case,  $P_w$  is identical to  $(BH)_{\max}$ .

## Means of magnetization

Permanent magnet needs to be magnetized after its fabrication. Magnetic field intensity should be at least triple the coercivity of magnetized material. Materials with low  $H_c$  value can be magnetized after assembling the circuit. Special electromagnets are typically used for magnetization of permanent magnets; their coils are powered by very strong pulse current. Other methods: discharge of condenser battery or application of special pulse power sources.

## Multi-pole magnetization

Basic type is the double-pole magnetization, i.e. magnet with one north and one south pole. This configuration allows the quick magnetization of block or cylindrical magnets (**axial magnetization**). Some magnets require use of multi-pole magnetization. For example, strips from magnetic rubber can thus generate higher holding force; in case of ring-like magnets for electric motors, the number of poles affects the smoothness and rotational speed. Multi-pole magnetization is facilitated by special configuration of field segments.

## Magnetic anisotropy

Suitable material must be chosen, if, for example, higher value of  $(BH)_{\max}$  product is required. In many cases, higher characteristics can be attained in similar, magnetically anisotropic material. This can be achieved during fabricating by strong field or magnetic tension with specific orientation. This way, directional structure is formed and subsequently the magnetically anisotropic properties manifest. The magnetic properties in the direction of the main magnetization axis are substantially stronger than in isotropic permanent magnet, the properties in perpendicular plane are hindered. To fully utilize the anisotropic magnet, it must be magnetized in the direction of the main axis.

## Curie temperature

When utilizing permanent magnets, close attention must be paid to operating temperature, so it does not exceed 0.4 of  $T_c$  [K] which is considered to be the „safe zone”.

## Irreversible changes

Thermal changes and deterioration of magnetization are caused by reversible and irreversible processes. Irreversible changes are closely related to the microstructure and magnetization mechanism of the material. The structure relaxes over time (also influenced by temperature) and the internal energy of the system decreases. Macroscopic consequence is **deterioration of magnetization**, eventually of other parameters.

## Surface treatment of magnets

### No surface treatment.

**Varnish.** Some types of magnets, especially metallic, are attacked by corrosion. If operated in normal conditions, synthetic varnish, powder varnish or nitro-varnish are sufficient to prevent this.

**Galvanic metal coating.** Magnets such as Fe-Nd-B and Alnico sometimes need to be coated with metal to provide sufficient corrosion resistance in aggressive environments, i.e. wet or warm atmosphere or in water. This coating must have good abrasion resistance, adherence to the surface and stable dimensions. Nickel coating is the most common type of galvanic metal coating.

## Classification of hard magnetic materials

Hard magnetic materials are, based on their **technical practice importance**, listed in this order:

- Malleable (formable) Fe-C steels with other alloying elements.
- Metal magnets from Al-Ni and Al-Ni-Co alloys, cast or sintered.
- Malleable alloys without carbon, Fe is not the predominating component.
- Magnets manufactured from very fine Fe powders possibly with added alloying elements or processed differently.
- Ferrite magnets based on  $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$  and others, ceramic and cemented.
- Other material types.

## Overview of hard magnetic materials

**Martensitic steel** is steel with martensitic structure reaching, even with addition of **tungsten, chromium, molybdenum** or **cobalt** maximum energetic product of  $(BH)_{\max}$  only  $4 \text{ kJ} \cdot \text{m}^{-3}$ . This significantly reduces the applicability of these materials.

**1. Metallic materials:** **martensitic steels with high internal stress** ~ quenched steels with martensitic structure  $\Rightarrow$  good magnetic properties can be achieved by aging steel with ~ 0.8 to 1.5 % C:  $B_r = 0.9 \div 1.2 \text{ T}; H_c = 1.6 \div 4 \text{ kA} \cdot \text{m}^{-1}$ .

### 2. Hard magnetic alloyed materials

**Tungsten steel** – (0.5 ÷ 1.1 % C; 1.5 ÷ 7 % W)  $\Rightarrow \uparrow H_c$ ,  $B_r = 0.9 \text{ T}, H_c = 4.8 \text{ kA} \cdot \text{m}^{-1}$ .

Drawback: aging, high cost,  $\downarrow$  magnetic properties.

**Chromium steel** – (0.8 ÷ 1.2 C; 2 ÷ 6 % Cr; 0.15 ÷ 1.5 % Si),  $B_r = 0.8 \div 1.05 \text{ T}, H_c = 4.4 \div 6 \text{ kA} \cdot \text{m}^{-1}$ .

More stable and cheaper than tungsten steel, but has worse magnetic properties.

Locally manufactured under brand name **Magnet C** and used for electricity meters, synchronous motors.

**Cobalt steel** – (1 % C; 2 ÷ 45 % Co; 2 ÷ 10 Cr; 0 ÷ 7 % W; 0 ÷ 2 % Mo).

$B_r = 0.75 \div 1.1 \text{ T}; H_c = 5.6 \div 23 \text{ kA} \cdot \text{m}^{-1}; \uparrow T_c, \uparrow$  magnetostriction, aging resistant.

**Molybdenum steel** – **Remalloy** (12 % Co; 17 % Mo).

### 3. Alnico alloys – cast magnets

Belong to the hardenable non-formable alloys of **Al-Ni-Fe** and **Al-Ni-Co-Fe** composition. Locally produced as “**Permag**” alloy. Al-Ni-Fe alloys have 12 to 15 % of aluminum, 24 to 28 % nickel and 57 to 63 % of iron. **Cu, Ti** or **Nb** are also added to enhance properties. Magnets from these alloys are produced by casting. Castings are difficult to grind. Solution treatment and hardening are essential parts of magnet thermal treatment. Al-Ni-Co-Fe alloys with lower amount of cobalt are magnetically **isotropic**. Increasing the cobalt content up to 25 % and thermal treatment in magnetic field increases the maximum  $(BH)_{\max}$  product, granting the material **anisotropic** properties.

Main alloy of this group is the **Fe-Al-Ni-Co** with excellent magnetic properties. Cast magnets have **directional crystalline structure**. Main alloying element is cobalt, aluminum, nickel and other elements, titan and copper on demand. There is a large variety of alloys designed with the intention to reduce (deficient) cobalt content, while maintaining satisfactory attributes for the given task. All employed alloys are very hard, brittle and can be worked basically only by grinding. Necessary presumption for optimal magnetic properties is the sand casting and subsequent thermal treatment (homogenization annealing at 950 to 1200 °C); the material precipitates in form of pin (small bar) ferromagnetic structure in crystallographic direction  $\langle 100 \rangle$ , thus creating good conditions for **directional magnetic anisotropy**. High Curie temperature also predetermines them for application at elevated temperatures.

**Table 4.7** Magnetic properties of Alnico alloys (iron based)

| Alloy type | Composition              | $B_r$ [T] | $H_c$ [ $\text{kA} \cdot \text{m}^{-1}$ ] | $(BH)_{\max}$ [ $\text{kJ} \cdot \text{m}^{-3}$ ] |
|------------|--------------------------|-----------|---|---|
| Alni       | Fe-Al-Ni-Cu              | 0.5 ÷ 0.7 | 32 ÷ 44                                   | 0.9 ÷ 1.4   |
| Alnico     | Fe-Al-Ni-Co-Cu           | 0.5 ÷ 1.4 | 44 ÷ 110                                  | 7 ÷ 34  |
| Alnico 2   | Fe-10Al-18Ni-13Co-5Cu    | 0.7       | 45  |   |
| Alnico 5   | Fe-8Al-13Ni-24Co-3Cu     | 1.2       | 49  |   |
| Ticonal    | Fe-Al-Ni-Co-Cu-Ti        | 0.7 ÷ 1.1 | 135 ÷ 155                                 | 24 ÷ 55   |
| Alnico 9   | Fe-8Al-15Ni-34Co-4Cu-5Ti | 1.0       | 125                                       |   |

**Characteristic** – alloys are brittle, non-formable. Magnets are produced by casting and powder metallurgy. Enhancement of magnetic properties → thermal treatment in strong magnetic field. Magnetic anisotropy is achieved (in some materials) by slow cooling in magnetic field around temperatures close to the melting point. Anisotropic alloys Al-Ni-Co with energetic product  $(BH)_{\max} = 45 \text{ kJ}\cdot\text{m}^{-3}$  can be produced this way; similar isotropic alloy only has  $(BH)_{\max} = 23 \text{ kJ}\cdot\text{m}^{-3}$ .

Formable magnetic hard materials (hardenable alloys) do not reach very high  $(BH)_{\max}$ , however their advantage lies in possibility of strip and wire production and the fact that they can be machined, pressed, bent etc. Formable hard magnetic materials are supplied as isotropic and anisotropic under brand names **Cunico**, **Cunife**, **Vicalloy**, **Platinax**, **Comol**, **Crovac** and others. The magnet needs to be able to be shaped for applications magnetic circuits of telephone speaker circuits, rotor of hysteresis motors, compass needles etc.

**4. Cunife alloys** – (Cu-Ni-Fe) 60 % Cu, 20 % Ni and 20 % Fe,  
 $B_r = 0.5$  to  $0.58 \text{ T}$ ;  $H_c = 35$  to  $47,8 \text{ kA}\cdot\text{m}^{-1}$ . Magnetically anisotropic.

**5. Cunico alloys** – (Cu-Ni-Co) 35 ÷ 60 % Cu; 20 ÷ 41 % Co  
 Cu50-Ni21-Co29 alloys achieve remanence of 0.35 to 0.5 T at  $H_c = 56 \text{ kA}\cdot\text{m}^{-1}$ . Fabricated in form of wires, strips, rods, or special shaped for small devices.

**6. Vicalloy** – (Fe32-Co52-V14) is processed by quenching, tempering and cold-forming. These alloys acquire their magnetic properties after forming. They were designed for demanding applications (watches, magnetic recorders, special motors, memory chips etc.). They have high remanence of 0.6 to 1.45 T at  $H_c = 36 \text{ kA}\cdot\text{m}^{-1}$ . Their price is very high due to high Co content.

**Table 4.8** Comparison of magnetic properties of alloys

| Alloy type | Composition  | $B_r$ [T] | $H_c$ [ $\text{kA}\cdot\text{m}^{-1}$ ] | $(BH)_{\max}$ [ $\text{kJ}\cdot\text{m}^{-3}$ ] |
|------------|--------------|-----------|---|---|
| Cunife     | Cu-Ni-Fe     | 0.5÷0.7   | 20÷40                                   | 3÷5   |
| Cunico     | Cu-Ni-Co     | 0.3÷0.5   | 36÷56                                   | 3,6÷4   |
| Remalloy   | Fe-Co-Mo     | 1         | 20                                      | 4÷5   |
| Vicalloy   | Co-Fe-V      | 0.9÷1.0   | 20÷40                                   | 4÷14  |
|            | Fe-Co-V      | 0.5÷0.8   | 15÷28                                   | 8   |
|            | Fe-Cr-Co (I) | 0.9÷1.1   | 31÷36                                   | 12  |
|            | Fe-Cr-Co (A) | 1.2÷1.3   | 43÷49                                   | 32  |
| Platinax   | Pt-Co        | 0.6       | 380                                     | 37  |

Note: (I) - isotropic, (A) - anisotropic

## **7. Fe-Cr-Co alloys**

These alloys can be fabricated into even very thin strips (up to 0.25 mm) and wires, thanks to their good cold formability. Forming also grants some alloys anisotropic properties – the magnetic attributes are significantly increased in the direction of forming. Thin strips of formable hard magnetic alloys are employed as miniature magnets for various applications: information displays, magnets of on-board units, indicatory elements, compasses. Thin strip semi-finished products can be fabricated into complex shapes by pressing, stamping, cutting and bending.

## **8. Other alloys**

Alloys without ferromagnetic properties represent another group of materials. Magnetic properties are attained by forming, preceded by quenching and followed by aging. Examples of such alloy are **Silmanal** (Ag89-Mn9-Al5) with remanence 0.05 T at  $H_c = 46 \text{ kA}\cdot\text{m}^{-1}$ , **Oertit** 900CP (Pt78-Cr22) remanence 0.65 T and  $H_c = 385 \text{ kA}\cdot\text{m}^{-1}$ . High cost limits their use to special applications (wristwatches, space devices).

## **9. Magnets produced by powder metallurgy**

Fine powders of **Mn-Bi**, (**alloys Fe**)–**Co** alloys are used for production of these magnets. The powder is pressed at 300 °C in magnetic field. Thus produced magnet is anisotropic. Oxide magnetic materials – **ferrites** – will be mentioned later.

Yet another group of materials for permanent magnet production is **metallic powder magnets**, allowing for the production of magnets with high dimensional precision without the need of exacting machining. These are, for example, sintered metallic magnets (type AlNi and Alnico) produced from pure Fe, Ni and Co. Aluminum needs to be added as an alloy with either iron, nickel or copper. Metal powders or alloys must be very pure with low carbon content. After mixing, grinding and sifting, the mixture is pressed and sintered at 1250 to 1330 °C. The sintering technology is suitable for small size magnet production.

Production technology of magnets from very fine powders with grain size comparable to the size of Weiss domains is very progressive. The mixture of powder and bonding agent is pressed in magnetic field. The grains turn, relatively to the external magnetic field, in the direction of spontaneous magnetization. The material thus attains high degree of **magnetic anisotropy**. The powders are produced from pure iron or Fe-35 % Co alloy. Best values were achieved with elongated shape grains. These magnets are sometimes referred to as ESD (Elongated Single Domain particles). Achievable attributes:  $B_r = 1 \text{ T}$ ,  $H_c = 95 \text{ kA}\cdot\text{m}^{-1}$  and  $(BH)_{\text{max}} = 25 \text{ kJ}\cdot\text{m}^{-3}$ .

## 10. Hard magnetic materials based on rare earth elements

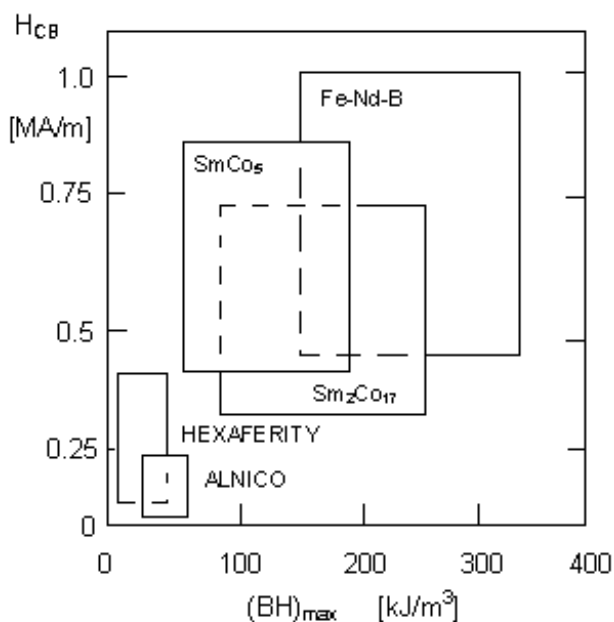
For production of permanent **cobalt – rare earth elements** magnets, rare earth element compounds (samarium, yttrium, lanthanum, cerium) and cobalt are used. Produced by powder metallurgy. Machined exclusively by grinding. Maximum energy product of these alloys is  $(BH)_{\text{max}}$  to 200  $\text{kJ}\cdot\text{m}^{-3}$ .

**Alloys of cobalt with rare earth elements of RCo<sub>5</sub> type**, where R is usually lanthanide (e.g. Sm, Pr, Nd and others) belong to the new generation of hard magnetic materials.  $\text{SmCo}_5$ ,  $\text{Sm}_2\text{Co}_{17}$  is the basic composition of this kind of material. Crystal lattice is **hexagonal with high degree of crystalline anisotropy**. The easy-magnetization direction is  $\langle 0001 \rangle$ . These compounds are very hard and brittle. Magnets are produced by **powder metallurgy**. They have excellent attributes, for example, the alloy  $\text{SmCo}_5$  has  $B_r = 0.9 \text{ T}$ ,  $H_c = 800 \text{ kA}\cdot\text{m}^{-1}$ ,  $(BH)_{\text{max}} = 250 \text{ kJ}\cdot\text{m}^{-3}$ . The size of these magnets can be greatly reduced because they can generate similar holding forces with much smaller dimensions, for example compared to ferrite magnets. Broader application of these magnets is limited mainly by the price of the ingredients, however the production technology is very demanding as well.

**Iron-neodymium-boron** with  $\text{Fe}_{77}\text{Nd}_{15}\text{B}_8$  composition.

**Table 4.9** Magnetic properties of hard magnetic rare earth element based materials

| Material                                     | Coercivity $H_c$ [ $\text{kA}\cdot\text{m}^{-1}$ ] | Remanence $B_r$ [T] | Max. energ. product $(BH)_{\text{max}}$ [ $\text{kJ}\cdot\text{m}^{-3}$ ] | Curie temperature $T_c$ [ $^{\circ}\text{C}$ ] |
|--|--|---------------------|---|--|
| <b>SmCo<sub>5</sub> 160/175</b>              | 680 ÷ 710  | 0.9 ÷ 0.925         | 160 ÷ 170   | 720  |
| <b>Sm<sub>2</sub>Co<sub>17</sub> 190/160</b> | 720 ÷ 790  | 1.03 ÷ 1.06         | 190 ÷ 215   | 825  |
| <b>Fe-Nd-B 210/160</b>                       | 780 ÷ 850  | 1.05 ÷ 1.12         | 210 ÷ 240   | 310  |
| <b>Fe-Nd-B 240/95</b>                        | 830 ÷ 870  | 1.13 ÷ 1.2          | 240 ÷ 265   | 310  |



Strong magnetic interaction (holding force) and small dimensions of rare earth element magnets are utilized in various applications. Such are, for example, rotors and stators in motors, linear motors, magnetic clutches and brakes, magnetic polarizers of liquids, magnetic separators, anti-theft systems in stores. Magnets based on rare earth elements are also used in automats and robots, automobiles, toys, kitchen appliances, washing machines, wristwatches, computing and others.

**Fig. 4.9** Comparison of magnetic materials regarding their  $H_{cB}$  and  $(BH)_{\text{max}}$

## 11. Single-crystal magnetic materials

Utilized in manufacture of **bubble memory**, **microwave devices** and **cores of reading heads for magnetic memory modules**.

**Magnetic composites** form their own separate group. They are fabricated from mixture of magnetic powders and plastic. Plastic can either just provide mechanical cohesion (in small amount) or give the composite plastic properties. Magnetic suspension of powders in suitable thinner and binding agent is used for production of active coatings of magnetic strips.

## **Application of permanent magnets**

### **Electrical engineering**

- Measurement and regulation** – galvanometers, ammeters, voltmeters, flux meters, photometers, tachometers, RPM gauges, watt meters, recorders, oscillation recorders, oscilographs, cardiographs, seismographs, pressure gauges, switching measurement devices.
- Motors and generators** – alternators, magnets of short-circuit motors, dynamos, DC motors, clock motors, ventilators, gyroscopes, pulse generators, dynamo ignition.
- Electro-acoustic and telecommunication** – pitch generators, telephone devices, devices for hard of hearing, pickups for string instruments, piezoelectric transducers, magneto phones, dictaphones, waveguides, directional isolators.
- Telecommunication** – speakers, vibration convertors, focusing units, correction components, switches, arc extinguishing.

### **Applied physics**

- Industrial application** – compass compensation, material separation, hardness measurement, polarity indicators, water softeners, solid particle filters.
- General application** – compasses, spring replacements, magnetic yoke.

### **Mechanics**

- Measurement and regulation** – flow meters, liquid level indicators, brakes of deviation devices, oscillation dampening .
- Connection devices** – switches, microscopes, magnetic connections, small pumps, mixers, over-a-wall propulsion, centrifugal connectors, polarized contacts, snaps-ons.
- Consumer goods** – calendars, cartotheques, lamps, signal lamps, magnetic seals, magnetic boards.
- Industrial application** – snap-on devices, conveyors, closing plugs, filters, separators, floor cleaners and sweepers, information and planning boards, friction brakes, screwdrivers, closing devices in refrigerators, furniture seals.

### **Other application**

- Medicine** – prosthesis, blood testing, removal of steel splinters, veterinary protection.
- Ceramic industry** – separators and solid particles strainers.
- Food industry** – magnetic locks, magnetic conveyors.
- Mechanical engineering industry** – snap elements, magnetic chucks and fixtures, oil filters.
- Metallurgy** – magnetic separators of metallic materials, conveyors.
- Automobile industry** – small engines, magnetic locks.
- Textile industry** – ball bearings of high-speed spindles.

## 4.5 OXIDE MAGNETIC MATERIALS

### FERRITES (magnetic oxide materials)

General formula: **MeO·Fe<sub>2</sub>O<sub>3</sub>** alias  $Me^{2+}O^{2-} \cdot 2Fe^{3+}3O^{2-}$ , where  $Me^{2+}$  could be:

Cd, Mg, Zn, Cu, Mn, Fe, Co, Ni, Ba, Sr and other elements.

**Ferrites are oxide materials** (ceramics) derived from ferric oxide **Fe<sub>2</sub>O<sub>3</sub>**. Their magnetism is facilitated by non-compensated antiparallel configuration of magnetic moments in domains (ferrimagnetics). Their crystal lattice is similar to inorganic materials of spinel, garnet or hexagonal structure (HCP). Crystal lattice of ferrite is very complex.

## **Properties:**

- High resistivity ( $10^2 \div 10^{10} \Omega \cdot \text{cm}$ ).
- Perfectly homogeneous.
- Negative coefficient of thermal resistivity.
- Low magnetic saturation.
- Low losses of electromagnetic energy, low eddy-current losses.
- Spinel structure ( $\text{MgO} \cdot \text{Al}_2\text{O}_3$ ) – complex cubic lattice structure.
- Magnetic properties – influence of d-electron spin of transition metal ions.
- Influence of cations distribution.
- Fe and other elements oxide compounds.

## **Classification of ferrites**

### **1. Soft magnetic ferrites with round hysteresis loop** (Me – Ni, Zn, Mn, Fe, Cu, Li, Mg, Co).

- Properties: - high structural and phase sensitivity to magnetic properties.  
Application: - 100 Hz to 100 MHz frequency range radio technology.  
- magnetostrictive materials for transformation of electromagnetic energy and mechanical oscillation.

### **2. Hard magnetic ferrites** (Me – Co, Ba, Pb, Sr).

- Properties: - high  $H_c$ , lower  $B_r$ , resistivity  $\sim 10^9 \Omega \cdot \text{cm}$ , brittle.  
Application: - permanent magnets, rotors, stators of small DC and asynchronous motors.

### **3. Ferrites with rectangular hysteresis loop** (Me – Mn, Mg).

- Properties: - high factor of rectangularity,  
- short change of magnetization time,  
Application: - computing (memory elements) and automated control systems.

### **4. Soft magnetic ferrites for very high frequencies** (Me - Ni+Cu, Mg+Mn, Ni+Zn, $\text{Y}_2\text{O}_3$ ).

- Requirements: - high density,  
- high resistivity  $10^8 \div 10^{11} \Omega \cdot \text{cm}$  (decrease of magnetic losses),  
- stability of properties in given temperature interval,  
- high precision in operation frequency range.  
Application: - waveguides.

### **5. Single crystal ferrites and their layers.**

- Properties: - ferromagnetic resonance,  
- homogeneous structure, low crystallographic anisotropy,  
- high density.

## **Technology of ferrite production – powder metallurgy**

Character of ferrites is very similar to that of ceramics – high hardness and brittleness. Ferrite production requires very pure raw materials (metal oxides). Total content of impurities cannot exceed 0.2 %, „ferrite poisons” Ba, Si and Na are especially detrimental. Raw materials are milled and mixed in a ball mill. The mixture is, after drying, calcinated in electric furnaces at 900 to 1100 °C, cations and anions diffuse and nuclei of ferrite form. These are subsequently crushed and grain size separated. Small size grains decrease permeability, large grains increase losses by eddy currents. Good quality ferrites have homogeneous grain size and small porosity. Bonding agent is then added to the mixture and the mass is pressed to desired shape. Stampings are dried in gas electric furnace. Final operation is sintering at about 1400 °C. The shape of the hysteresis loop can be adjusted by thermo-magnetic treatment. Cooling in magnetic field produces material with constant permeability hysteresis loop or with rectangular hysteresis loop. Machining of ferrites is very difficult, since they are very hard and brittle. Applicable machining technologies are: grinding, ultrasound machining or diamond cutting. However, powder metallurgy products have precise dimensions, so the machining is often unnecessary.

## **1. Soft magnetic ferrites**

### **Spinel ferrites**

These have  $\text{MeO} \cdot \text{Fe}_2\text{O}_3$  structure type. Most important are the  $\text{MnO} \cdot \text{Fe}_2\text{O}_3$  ferrites.

- Mixture ferrites:** two-component -  $\text{MnO} \cdot \text{ZnO} \cdot 2\text{Fe}_2\text{O}_3$ ,  $\text{NiO} \cdot \text{MnO} \cdot 2\text{Fe}_2\text{O}_3$ ,  $\text{CuO} \cdot \text{ZnO} \cdot 2\text{Fe}_2\text{O}_3$ ,  
three-component -  $\text{MgO} \cdot \text{MnO} \cdot \text{NiO} \cdot 2\text{Fe}_2\text{O}_3$ .

**Telecommunication** has the highest requirements on magnetic properties of soft magnetic ferrites. It requires materials with highest possible permeability, low loss factor, low hysteresis losses and others. All these requirements are met by Mn-Zn ferrite. Initial permeability  $\mu_i$  of industrially produced ferrites is in range between 10 to 10000.

**Table 4.10** Characteristic properties of Mn-Zn and Ni-Zn ferrites

| Ferrite   | $\mu_i$ | Density<br>[ $\text{kg}\cdot\text{m}^{-3}$ ] | $J_S$<br>[T] | $H_c$<br>[ $\text{A}\cdot\text{m}^{-1}$ ] | $T_c$<br>[ $^{\circ}\text{C}$ ] |
|---|---------|--|--------------|---|---------------------------------|
| $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ | 1500    | 4900   | 0.35         | 16  | 100                             |
| $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ | 250     | 4500   | 0.42         | 56  | 250                             |

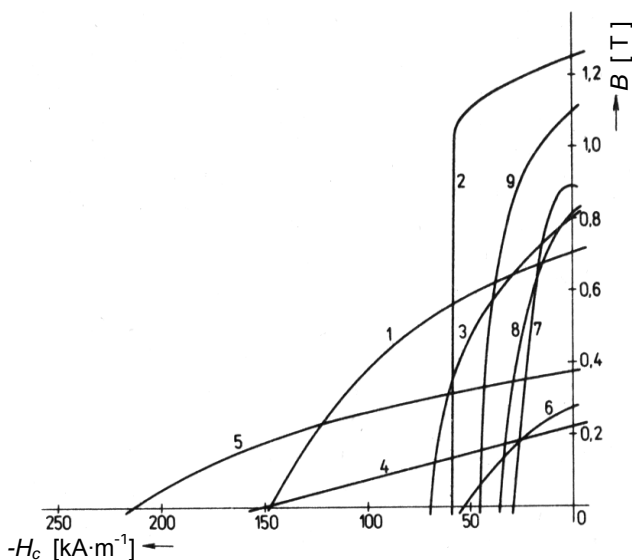
In the last years, materials with guaranteed resistivity of  $10^5 \Omega\cdot\text{m}$  have been added to the spectrum of soft magnetic ferrites products. Those are Mg-Mn-Zn ferrite for **cores of deflection coils for color screens**.

### Application of soft magnetic ferrites:

High-frequency electrical engineering (Mn-Zn, Ni-Zn), miniaturization and radio-electronics, microwave technics (core of wide spectrum, inter-frequency, external and pulse transformers, recording heads of tape recorders, cores of high-frequency telecommunication transformers, ferrite antennas, magnetic amplifiers, deflection coils of cathodic tubes in television).

## 2. Hard magnetic ferrites - hexagonal ferrites

Hexagonal ferrites with magneto-plumbite structure have the  $\text{MeO}\cdot 6\text{Fe}_2\text{O}_3$  composition, where Me is Ba, Sr, Co or Pb. Hexagonal lattice is characteristic for its high anisotropy in the  $\langle 0001 \rangle$  direction. Commonly used ferrite is the  $\text{BaO}\cdot 6\text{Fe}_2\text{O}_3$ , with portion of Ba atom replaced with Co, Ni, Mg and so on. High resistivity of ferrites helps to minimize the eddy current losses. Low remanence decreases the hysteresis losses (with steep magnetization curve) which is favorable for component miniaturization. Anisotropy of magnetic hard ferrites is achieved by pressing the semi-finished products in magnetic field. The anisotropy is so distinctive that the material also exhibits different mechanical and thermal properties in the anisotropy axis. Local hard magnetic materials were produced under brand name **Durox** by Pramet Šumperk in the Czech Republic.



**Fig. 4.10** Demagnetization curves of various hard magnetic materials

## 3. Magnetic composites

Magnetic composites consist of fine-grained ferromagnetic or ferrimagnetic material and suspension medium. Suspension medium is usually natural or synthetic resin, or thermally hardened granulate. Oldest composite was so called high-frequency iron. There are two groups of these composites. The organic material in the first group works only as a bonding agent, organic material in the second one also substantially affects the properties of the composite (so called magnetic rubber).

Hard magnetic ferrites pressed with **plastic** belong to the **first group**. **Bakelite ferrite** is produced from formaldehyde resin. Their advantages are precise dimensions of the product and good machinability. Polyethylen-ferrite, shortly **pefer**, is an agglomerate of branched polyethylene and fine-ground ferrite powder. Content of ferrite powder is chosen so it could be shaped by injection by common spraying machines. Injection products are precise and do not need to be machined, they are only magnetized. This process is suitable for low-cost production of large batches of same magnets.

**Magnetic rubbers** belong to the **second group**. They are produced by mixing of **flexible bonding agent** (thermoplastic resin or rubber) and powder with permanent magnet properties. This causes certain deterioration of magnetic energy per unit of volume, however complex shapes or thin magnets can be produced this way. Magnets are characteristic for their elastic properties and are fabricated in form of flat plates or strips with 2 to 5 mm thickness. Arbitrary shapes can be cut from plates. Shaped pressings can also be produced. The composite is

required to maintain its elastic properties, typical for natural rubber. Rubber is usually filled with hard magnetic ferrite powder and processed by rolling and calendaring. Repeated rolling arranges the ferrite grains so the bulk material is anisotropic. Magnetic rubbers can be used immediately, or shaped by cutting, strip cutting, drilling, lathing and others.

### Properties of magnetic composites

Plastic magnets are relatively soft, and, if rubber bonding agent is used, also elastic. The density of the material is slightly higher than common pure plastic or rubber, roughly  $3.2$  to  $4.5 \text{ kg}\cdot\text{dm}^{-3}$ . Magnetic properties depend on the type of used magnetic powder – either ferrite powders or materials based on rare earth elements.

### Application of magnetic composites

Magnetic composites, produced from mixture of barium ferrite and polyethylene are nowadays utilized in less demanding applications (magnetic locks, magnetic rubber fridge seals), but also for speaker membranes, color correction magnets in monitors, magnetic switches, magnetic connectors, rotors and stators of small motors and others. Application of magnetic varnishes and glues is also growing. Magnetically active layers of magnetic strips also belong to this group. Thin profiles, strips and belts are utilized as metallic surfaces snap-ons, for advertisement of information racks. Complex products – e.g. component with axis, cogwheel etc, can be produced by injection or hot pressing.

## 4. Ferrites with special properties

These are ferrites for special application with different chemical composition. Examples are microwave ferrites with garnet structure, ferrites with rectangular hysteresis loop, magnetostriction ferrite and compact ferrites for recording heads.

Production of these ferrites is highly demanding – especially on chemical purity of raw materials, degree of oxidization, homogeneity and grain size. Chemical purity is achieved by careful choice of raw materials and refining process. Salt solutions (oxalates, formates) are sometimes used – they are mixed in stoichiometric ratio, evaporated and transferred to oxides by annealing. The desired chemical composition is normally achieved by mixing pure oxides produced by annealing at defined temperature in nitrogen atmosphere with suitable oxygen vapor pressure.

## 5. Bubble memory materials – magnetic garnets (ferrite garnets)

These are single crystal, ferromagnetic materials containing rare earth elements and ferromagnetic gallium or iron. Magnetically anisotropic materials with low magnetization are an environment for highly-mobile cylindrical domains („bubbles”). Their general formula is  $3\text{Ln}_2\text{O}_3\cdot 5\text{Fe}_2\text{O}_3$ , resp.  $\text{Ln}_3\text{Fe}_5\text{O}_{12}$ , with Ln being either yttrium or rare earths Gd, Eu, Tb etc. except Nd, Pr, La and Ce which do not form stable garnet in sufficient amount. The layer must be nearly flawless for successful application – flaws hinder or deviate the domains from their trajectory (e.g. dislocations, impurities, cracks, magnetic powder).

Active magnetic element is fabricated by epitaxy of coating of yttrium-iron garnet (**YIG**). The coating is isothermally grown from liquid phase on single crystal non-magnetic substrate from gadolinium-gallium garnet (**GGG**) with similar lattice constants. Single crystal **GGG** is produced by drawing of melt metal (Czochralski method) in nitrogen atmosphere with 2 % oxygen addition. The crucible is made of iridium. Cutting, grinding and polishing of plates is very similar to the processing of semiconductors. High-quality single crystal with low concentration of defects is achieved by computer controlled drawing from melt metal.

Used in microwave technology and for production of magnetic bubble memory.

## 6. Materials with magnetostriction properties

Ferromagnetic material **changes its dimensions** during magnetization without changing its volume. This phenomenon is called magnetostriction. Mechanical stress also changes the character of hysteresis loop. Magnetostriction factor depends on intensity of magnetic field and reaches stable value at saturation. Magnetostriction is typical for all ferromagnetics. Magnetostriction properties are distinctly anisotropic. Some materials exhibit positive, other have negative magnetostriction. These are doped Ni or Ni-Cu ferrites. Addition of cobalt decreases the thermal dependency of resonance frequency. Two kinds of these ferrites are being produced:

Magnetostrictive ferrites for resonators are the main component of all electro-mechanic filters in radio-technology. They have higher selectivity than commonly used LC circuits.

Magnetostriction ferrites for converters are employed in generators and detectors of ultrasonic waves.



## **7. Ferrites with rectangular hysteresis loop**

Certain types of Mg-Mn-Zn and Li-Ni-Zn exhibit spontaneous rectangular hysteresis loop. Suitable processing technology produces material with higher degree of hysteresis loop rectangularity than Ni-Fe alloys. These are utilized in computing in shape of various-shaped toroids and in memory matrix fabrication. The tilt time was reduced 40 times by employing ferrite cores instead of metallic foils. Another increase in computer performance can be achieved by reducing the size of ferrite core.

The advantage of ferrite memories is their radiation resistance which is the major drawback of silicon based semiconductors. These are thus still relevant for some military application.

Although the core magnetic memories are nowadays replaced by semiconductive components with higher memory density, the ferrites are employed if one of these advantages can be utilized:

- high recording density,
- information storage without an external power source,
- no alteration of stored data in case of power shortage,
- very low energy necessary to store and read the information.

## **8. Ferrites for recording and reading heads**

These materials are required not only to have very good magnetic properties, but also very low porosity. The goal is to achieve density corresponding to that of single crystal. Another requirement is good machinability, enabling production of flawless edges and surface roughness after lapping. This is why Ni-Zn and Mn-Zn ferrites are utilized.

Functional gaps in recording heads are wide and narrow. Narrow gaps are necessary for modern high-capacity disc recording and image recording. Their size is comparable to the size of ferrite pores. Reduction of porosity is achieved by either:

- adjustment of common production technology focused on pore reduction. The porosity can be thus reduced from 5 % to 1 %. This material can be used for less demanding applications.
- simultaneous effect of temperature and pressure during component pressing at 1200 to 1300 °C. This reduces the porosity to 0.1 %. Process must be individually adjusted and the pressings are difficult to machine.

Common classification puts these materials to the hard magnetic, but also soft magnetic material group; application type and other specific requirements set them apart. Principle of magnetic recording lies in dividing the binary signal to two magnetization levels and then reliable recording that on recording medium. Reading of the recording is facilitated by scanning the magnetization and its conversion to electrical signal. Currently, the data are usually recorded as digital signal. High level of magnetization is achieved in recording heads which are fabricated from soft magnetic material; they can record, read, but also delete the information. Recording material is ferro- or ferrimagnetic, their coercivity goes as high as 25 to 100 kA·m<sup>-1</sup>. Another difference is that they are utilized in form of fine particles dispersed in organic medium or as a thin layer. Besides other methods, they are prepared by chemical methods (e.g. electrolysis), not by metallurgical processes. Considering the demand of miniaturization, the density of recording is very important – it depends on the material and its form.

### **a. Materials for magnetic tapes and discs**

During recording, the layer is in close proximity to the gap in the recording head. Dispersion field of the gap, produced by the excitation signal, magnetizes the layer using two different levels of magnetization. Magnetized regions retain the information until another recording cycle or until deleted. During the recording, the layer is the source of magnetic flow changes in induction heads or resistance changes in magneto-resistive heads. Magnetic properties requirements on recording material are:

- high saturation induction (thus high values of magnetization),
- high coercivity (stable recording),
- high degree of rectangularity of the loop (good differentiation of magnetization levels),
- high resistivity of the layer (reduces eddy-current losses and reduces the size of magnetized regions).

These requirements are in present day met by powder oxide ferrites and metallic ferromagnetics in the form of thin layers.

**Powder materials** are utilized in form of single domain rods of submicron size. Along with plastic bonding agent (plastic), they form thin layer on plastic strip, flexible or firm disc (Al). The particles present about 40 % of the volume of layers. Most common powder materials are listed in Table 4.11.  $\gamma$  Fe<sub>2</sub>O<sub>3</sub> has cubic lattice structure, in the case of Co-Fe<sub>2</sub>O<sub>3</sub> is the powder surface doped by cobalt, annealed and portion of the Fe atoms in the surface layer is replaced by Co atoms (3 ÷ 4 %).

**Table 4.11** Properties of ferrites for magnetic recording

| Material                    | Fe <sub>2</sub> O <sub>3</sub> | Cr <sub>2</sub> O <sub>3</sub> | BaO · 6Fe <sub>2</sub> O <sub>3</sub> | Co-Fe <sub>2</sub> O <sub>3</sub> | Fe          |
|-----------------------------|--------------------------------|--------------------------------|---------------------------------------|-----------------------------------|-------------|
| $H_c$ [kA·m <sup>-1</sup> ] | 28                             | 55                             | 160                                   | 60                                | 130         |
| $B_s$ [T]                   | 0.5                            | 0.6                            | 0.3                                   | 0.25                              | 1.3         |
| Form                        | stick                          | stick                          | plate                                 | stick                             | stick       |
| Size [μm]                   | 0.3 x 0.6                      | 0.5 x 0.005                    | 0.1 x 0.025                           | 0.3 x 0.006                       | 0.3 x 0.005 |

**Materials utilized in the form of thin layers** are deposited on non-magnetic substrate of less than micrometer thickness. These have polycrystalline character and domain size is smaller than grains. Grain boundaries hinder the movement of domain walls and thus increase coercivity. Unlike the powder materials, the concentration of ferromagnetic material in the thin layer is much higher which corresponds to higher saturation induction. Big drawback is its price and complicated fabrication technology – vacuum vapor deposition or sputtering. The layers are fabricated from the basic ferromagnetic materials (Fe, Ni, Co) their alloys with rare earths and ferromagnetic oxides.

### **b. Materials for magneto-optic recording**

Magneto-optic recording is one of the most purpose-full method how to store data on solid replaceable discs. This method utilizes the properties of the given material around Curie point. At this temperature, the material has very low coercivity (good ability to store the magnetic information). Coercivity decreases to less than 1/10 compared to the coercivity at 20 °C. Changing the magnetization is therefore easy and does not require strong magnetic fields.

Focused beam of infrared laser diode is used for recording (wavelength of emitted beam 830 nm). Recoding on disc is a thermo-magnetic process. Magneto-optic layer on the surface of the disc is locally heated by pulse (for about 500 ns) laser with about 10 ÷ 20 mW power. After this, the information is recorded by magnetic field  $H$ . During the cooling of the layer, the coercive field  $H_c$  disappears and effective magnetization field  $H_{ef}$  (stronger than  $H_c$ ) records the information.  $H_{ef}$  consists of inner demagnetization field and the functional field. The direction of remanent magnetization corresponds to the field  $H_{ef}$ .

Amorphous rare earth alloys (20 % Gd or Tb) with ferromagnetic metals Fe and Co are commonly used. These are prepared by cathodic sputtering. Other perspective materials are garnets ( $T_c = 160$  °C) and Co-Pt, Co-Ca alloys, operating at frequency above frequency of visible with  $T_c = 250 ÷ 400$  °C.

Up to this date, amorphous alloys, such as Gd-Tb-Fe or Tb-Fe-Co are utilized in commercial magneto-optic discs as memory medium. High-density and multi-layer recording materials are candidates for the near future. Multilayered Co/Pt disks have more controllable perpendicular magnetization and also 100 % remanence. Co/Pt films offer higher corrosion resistance and wider rotation angle with beam of narrower wavelength (300 ÷ 400 nm) which enables higher recording density when using blue light laser recording diode.

Co-Ni/Pt materials were developed for magneto-optic media, since their Curie temperature and  $T_c$  are lower than those of Co/Pt material. Lower  $T_c$  is required for more reliable low-power recording along with high number of R/W (read/write) cycle.

Computers are equipped with **optical drives**, utilizing laser light or electromagnetic waves close to the visible light for part of the data reading and recording. It's a periphery used for data storage on optical discs. Most of the drives can also record data. The recorders are also called burners or writers. Optical disc drives are utilized for data archiving or exchange. Along with flash memories, they replaced the floppy discs and tape recorders. The essential parts of optical recording drive are: **semiconductor laser**, **laser focusing lens** and **photodiode** which receives the light reflecting from the disc surface. Laser light wavelength for **CD** is 780 nm, for **DVD** 650 nm and for **Blu-ray** in **HD DVD** 405 nm. Basic principle of burning is same for all systems. Single-recordable disc has a polycarbonate substrate with deposited gold layer. Laser beam burns through the polycarbonate and stops at the gold layer, thus creating a pit.

# 5. HIGH PURITY MATERIALS

New areas of advanced science and technology, for example, semiconductors, microelectronics, optoelectronics, superconducting materials, vacuum technology, nuclear metallurgy, space industry and technology, require materials, metals and their special alloys and compounds with high chemical purity and defined physical and structural parameters and specific applied properties. These can be found and achieved mainly in high purity substances and elements with the basic **purity** of the order of **99.9999 %** and higher, i.e., with the total content of impurities and **admixture below  $10^{-4}$  %** and lower.

**A pure substance** is a physically and chemically homogeneous substance or a chemical compound consisting of a specific type of atoms or ions or molecules and having only its own typical complex of constant properties.

The increase of the importance of high purity substances has been the result of the development of new areas of technology, for example, nuclear technology, aerospace and also microelectronics and optoelectronics, with special techniques of wave transfer and energy quanta and also memory or other properties of pure substances. In these special areas it is not possible to ignore materials defined with respect to purity, not only chemical, but also physical, dislocation-free, structural, nuclear, semiconductor, isotope, etc. Taking into account the areas of application, this type of purity can often be defined more easily as the **purity for a purpose**.

The purity for a purpose is defined from the viewpoint of the presence of impurities unsuitable or, on the other hand, suitable for obtaining the given or required properties. For example, silicon, used for **semiconductor applications**, must contain a minimum concentration of admixtures of the first, second, third, fifth and sixth group of the periodic table of elements, and the relatively high concentration of admixtures of the fourth group (Ge) is not harmful, because this element does not have any significant negative effect on the electrical and semiconductor properties of the main element. In the case of artificially prepared single crystals, it is necessary to evaluate their **structural perfection**, the angle of disorientation of grains and the density and distribution of dislocations.

## Methods of the description of purity

The chemical purity of metals or the concentration of admixtures in the range of pure metals is described by a nine-point system proposed by **van Arkel**:

| Designation | Purity (%) | Impurity content (%) |              |
|-------------|------------|----------------------|--------------|
| 1 N         | 90 - 99    | 10 - 1               |              |
| 2 N         | 99         | 1                    |              |
| 3 N         | 99,9       | 0,1                  | 1000 ppm     |
| 4 N         | 99,99      | 0,01                 | 100 ppm      |
| 5 N         | 99,999     | 0,001                | 10 ppm       |
| 6 N         | 99,9999    | 0,0001               | <u>1 ppm</u> |
| 7 N         | 99,99999   | 0,00001              | 100 ppb      |
| 8 N         | 99,999999  | 0,000001             | 10 ppb       |
| 9 N         | 99,9999999 | 0,0000001            | <u>1 ppb</u> |

The designation of the concentration of impurities in **ppm**:  $1 \text{ ppm} = 10^{-4} \%$  of admixtures, i.e. the purity at which for 1 million ( $10^6$ ) atoms of the main substance there is only 1 atom of the admixture. For even lower concentrations, it is necessary to use the term **ppb**, i.e. parts per billion;  $1 \text{ ppb} = 10^{-7}$  of admixtures, i.e. for 1 billion ( $10^9$ ) of the atoms of the main substance there is 1 atom of the admixture.

Another method of definition of purity, in particular in semiconductor technology, is the unit  $\text{cm}^{-3}$  which expresses the total number of the atoms of impurities and admixtures in  $1 \text{ cm}^3$  of the main semiconductor. The current requirements on the silicon suitable for microelectronics permit the maximum total content of  $10^{14}$  of all atoms of the admixtures in  $1 \text{ cm}^3$  of silicon, which represents the purity of approximately 8 N, i.e. 10 ppb of the present impurities. Silicon with a diamond-like structure has a lattice constant of  $a = 5.429 \cdot 10^{-10} \text{ m}$ , which represents a total of  $5 \cdot 10^{22}$  of silicon atoms in  $1 \text{ cm}^3$ . After doping with 1 ppm of a dopant (micro-alloying addition),  $5 \cdot 10^{16}$  atoms of the admixture penetrate into Si. In this case, only 1 atom of the dopant is available for 1 million atoms of Si. For the given purity of semiconductor Si of 8 N only 'one' atom of the harmful impurity is permissible for 'one hundred million' of Si atoms.

## GENERAL CHARACTERISTICS AND CLASSIFICATION OF METHODS OF SEPARATION AND REFINING OF SUBSTANCES

In order to obtain high-purity metals and semiconductor compounds, it is necessary to carry out deep refining of the main component to remove admixtures. Therefore, it is essential to use the efficient combination of the methods based on **different physical, chemical and physical-chemical properties of substances**, ensuring the separation of impurities and admixtures from the main compound. Below, we propose the classification of the main processes of refining metals and certain substances to remove impurities and admixtures. In this **classification of the refining procedures** for the separation and refining of substances, the processes are divided into groups 1 to 8 on the basis of the physical-chemical properties utilised in the separation of components.

### **1. Sorption**

- adsorption
- ion exchange
- chromatography

### **2. Extraction**

- liquid extraction

### **3. Crystallisation**

- crystallisation from solutions
- crystallisation from melts
- directional crystallisation\*
- zone melting\*
- freezing-out

### **4. Evaporation and condensation**

- sublimation
- distillation
- rectification\*
- distillation by means of transport chemical reactions\*

### **5. Electrolysis**

- electrolytic precipitation with preliminary cleaning of the electrolyte\*
- electrolytic refining\*
- amalgamation electrolysis\*
- electric transfer\*

### **6. Diffusion**

- diffusion
- thermal diffusion
- high-voltage dialysis

### **7. Selective precipitation, oxidation and reduction**

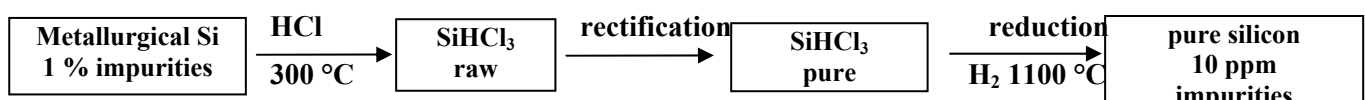
- selective precipitation
- selective oxidation and reduction

### **5. Removal of gases**

- vacuum extraction
- electron beam melting\*

Comment: the processes indicated by \* are used for higher degrees of refining.

As an example of the gradual process of silicon refining with final purity 5N (99.999 % Si) you can see the schema:



SiHCl<sub>3</sub> – trichlorsilane (low-boiling liquid)

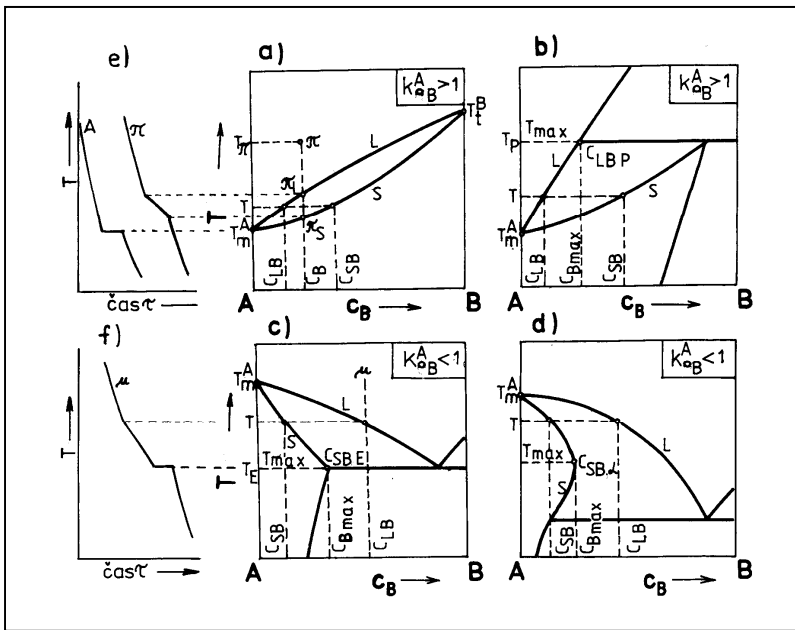
Rectification – repeated distillation

# 5.1 DISTRIBUTION COEFFICIENT IN CRYSTALLISATION

Crystallization from the melt is the process of transition of metals and alloys from the liquid L (melt) to the solid state (crystal). **The kinetics of the crystallization processes** consist from two independent phenomena:

- Nucleation, i.e. formation of crystallization nuclei (homogenous or heterogeneous nucleation);
- The crystal growth, i.e. the rate of displacement of the different types of crystal – melt interface (planar, cellular, dendritic) in relation to the temperature gradient.

The concentration conditions in the process of solidification of alloys can be evaluated by means of the appropriate equilibrium diagrams of binary or poly-component systems. The existence of a temperature difference between the liquidus and solidus, Fig. 5.1, indicates that at every temperature in the given range the solid and liquid phases with different chemical compositions are in thermodynamic equilibrium. This shows that the process of solidification is accompanied, at the crystal–melt boundary, by the distribution of the impurities and admixtures between the two phases. Assuming that the admixture is characterised by unlimited solubility in the melt and in the solid phase (Fig. 5.1a), the composition of the two phases changes continuously during the solidification process, and the equilibrium between them is represented by the solidus and liquidus curves in the A–B binary system or by appropriate areas of the poly-component systems.



**Fig. 5.1** Main types of binary diagrams and solidification curves  
 a) Unlimited solubility (ideal type),  
 b) Peritectic type,  
 c) Eutectic type,  
 d) Retrograde solubility of the solidus curve,  
 e) Curve of cooling the pure substance A and alloy  $\pi$ ,  
 f) Curve of cooling for alloy  $\mu$  in the case of the eutectic reaction.

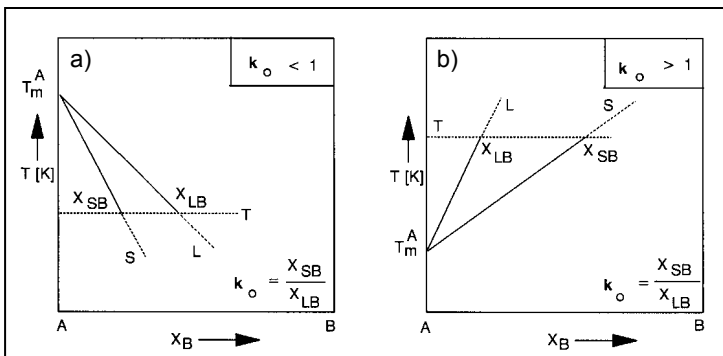
## a) Equilibrium distribution coefficient in crystallization

The measure of distribution of the admixtures between the solid and liquid phase is the **equilibrium distribution coefficients**  $k_{oB}^A$  of the admixture B in the main substance A, defined as the **isothermal ratio** ( $T = T_S = T_L$ ) of the concentration **of the admixture element B in the solid phase**  $X_{SB}$  (solidus) **and in the liquid phase**  $X_{LB}$  (liquidus):

$$k_o = k_{oB}^A = X_{SB} / X_{LB}, \tag{5.1}$$

where  $X$  the concentration is given in molar fractions or in atomic %.

The equilibrium distribution coefficient is lower than 1,  $k_{oB}^A < 1$ , for systems in which the admixture element B decreases the melting point  $T_m^A$  of the main component A, Fig. 5.2a – eutectic systems. For the systems in which the admixture element B increases the melting point, the distribution coefficient is higher than 1,  $k_{oB}^A > 1$ , Fig. 5.2b.



**Fig. 5.2** Definition of the equilibrium distribution coefficients  
 a) Admixture B reduces melting point  $T_m^A$  ( $k_o < 1$ ),  
 b) Admixture B increases melting point  $T_m^A$  ( $k_o > 1$ ).

The different solubility of the admixtures and impurities in the liquid and in solid phase leads to re-distribution of the admixture (B) in matrix (A). This results in the formation, in every primary crystallisation, of different **segregation micro- and macro-heterogeneities** with a negative effect on the properties of solidified substances. The above-defined distribution coefficient is the **main material parameter for the refining of substances by crystallisation processes**, such as zone melting and directional solidification, being selective crystallisation processes. Generally, it may be concluded that as the distance of  $k_o$  from unity increases, the efficiency of refining of metal to remove the given admixtures in solidification refining processes is higher.

### b) Interphase (kinetic) distribution coefficient

In the real crystallisation process, there is **no thermodynamic equilibrium of the individual phases** at the crystal–melt interface. The phase transformation takes place at a specific rate so that the liquid and solid phases are characterised by the presence of concentration gradients, and the temperature at the interface is somewhat lower than the equilibrium temperature.

The phase boundary is characterised by the occurrence of two processes, i.e. the actual phase transformation and the transport processes of the participating phases (mass and energy transfer). In the solidification of pure metals and the majority of other substances, the rate of crystallisation determines the removal of latent heat from the interface. The admixtures with  $k_o < 1$ , which are implanted in the crystal during solidification with a lower concentration in comparison with the liquid phase, enrich the melt in front of the phase boundary and must be transported into the main volume of the liquid phase. The behaviour of the admixture element B at the crystal–melt phase boundary is described by the so-called **interphase or kinetic distribution coefficient**  $k_{kin}$ :

$$k_{kin} = C_{S(o)} / C_{L(o)}, \quad (5.2)$$

where  $C_{S(o)}$ ,  $C_{L(o)}$  is the concentration of admixture in crystal (resp. in melt) at the phase boundary.

The kinetic distribution coefficient also depends on the morphology of the atomically smooth or atomically rough (diffusion interface) phase boundary and on the crystallographic orientation of the growth areas, facets and growth nuclei.

### c) Effective distribution coefficient

The processes taking place during crystallisation at the interface between the liquid and solid phases result in changes of the concentration in the melt in the immediate vicinity of the interface. The concentration of the admixture in the melt is equalised by the effect of different types of convection in the main volume of the melt and by diffusion in the limiting layer with thickness  $\delta$ . The relationship for the **effective distribution coefficient** of the admixture in the main substance was derived by Burton, Prim and Slichter from the equation of continuity and for suitable boundary conditions:

$$k_{ef} = \frac{k_o}{k_o + (1 - k_o) \exp \frac{v\delta}{D_L}}, \quad (5.3)$$

where  $v$  – the macroscopic speed of movement of the phase boundary ( $\text{cm}\cdot\text{s}^{-1}$ ),

$\delta$  – the thickness of the sub-laminar diffusion layer (cm),

$D_L$  – is the diffusion coefficient of the admixture B in the melt ( $\text{cm}^2\cdot\text{s}^{-1}$ ).

The theory proposed by Burton, Prim and Slichter assumes that the solidification front is characterised by the formation of a thin diffusion layer  $\delta$  whose thickness changes in relation to the intensity of mixing the melt. The thickness of this layer also depends on natural convection and viscosity of the melt, and the speed of rotation of the crystal (forced convection) and on the nature of the flow in the melt (turbulent or laminar) and only to a certain degree on the crystallization rate.

Equation (5.3) indicates that at the growth rate  $v = 0$  the value  $k_{ef} = k_o$  which means that as the solidification rate decreases, the degree of enrichment by the impurity in the melt for the case in which  $k_o < 1$  increases. At the rate  $v = \infty$ ,  $k_{ef} = 1$ , and there is no distribution of the admixture in the macro-space of the ingot. The effective distribution coefficient can be determined by experiments and is described by the following equation:

$$k_{ef} = C_{S(o)} / C_{L(\infty)}, \quad (5.4)$$

where  $C_{L(\infty)}$  is the concentration of the admixture B in the main volume of the melt.

In order to ensure that the process of refining of the main substance to remove the admixture is efficient, it is necessary to select the minimum possible speed of movement of the solidification interface and to reduce the thickness of the diffusion layer  $\delta$  it is necessary to increase the intensity of forced convection of the melt (by

mixing the melt by electromagnetic methods, high frequency current, mechanically, or by rotating the crystal and the melt, etc).

## 5.2 REFINING CRYSTALLIZATION METHODS

At the present time, the processes of crystallisation from the melt occupy one of the most important areas in the group of the methods of refining metals and semiconductors. They are used in the final stage of refining for the removal of very small and trace amount of admixtures.

The refining methods, based on the processes of crystallisation from the melt, include:

- Directional crystallization,
- Zone melting,
- Drawing of crystals and single crystals from the melt.

### 5.2.1 Directional crystallization

Directional crystallization is a refining method based on the distribution of admixtures between the solid and liquid phases. The method is based on the fact that the crystal–melt phase boundary moves slowly through the molten ingot of the refining material with the length  $l_0$  at the initial concentration of the admixture  $C_0$  (Fig. 5.3). In this case, the solidifying interface is characterised by the **distribution of impurities and admixtures present in the basic substance**.

The concentration profile of the admixture in the solidified part  $C(x)$  depends on the change of the concentration conditions at the phase boundary which are given mainly by the values of the distribution coefficients of the individual admixtures present in the main refining substance. The relationship between the distribution coefficient, the amount of the solidifying substance and the concentration of the admixture was published by the W.G. Pfann for directional crystallization in the following form:

$$C(x) = C_0 k (1 - g)^{k-1}, \quad (5.5)$$

where  $C(x)$  - the concentration of the admixture in the distance  $x$  from the beginning of the crystal;  
 $C_0$  - the initial concentration of the admixture in the entire volume of the melt;  
 $k$  - the distribution coefficient of the element B in the main substance A;  
 $g$  - the relative part of the solidified crystal ( $g = x/l_0$ ),  $x$  the distance from the beginning of the ingot.

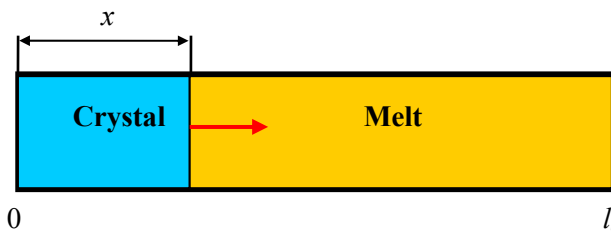
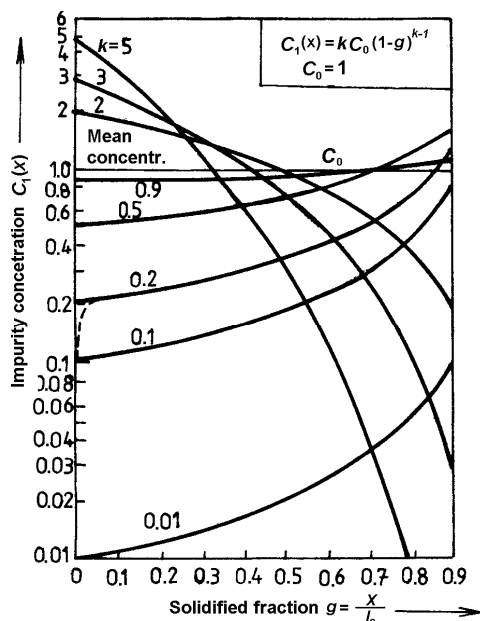


Fig. 5.3 Principle of directional crystallization



In the derivation of the equation, Pfann use the following assumptions:

- The diffusion of admixture  $D_{LB}$  in the melt is complete and ideal;
- The diffusion of admixture  $D_{SB}$  in the solid phase is equal to zero;
- The admixture forms a solid solution with the main substance;
- During solidification, the density of the material does not change ( $\rho_S / \rho_L = 1$ ).

At  $x = 0$ , the newly formed concentration is  $C(x = 0) = C(0) = C_0 k$ . As the distance of the value of the distribution coefficient from 1 increases ( $k \ll 1$ ,  $k \gg 1$ ), the distribution efficiency of the given admixture in the entire volume of the ingot increases.

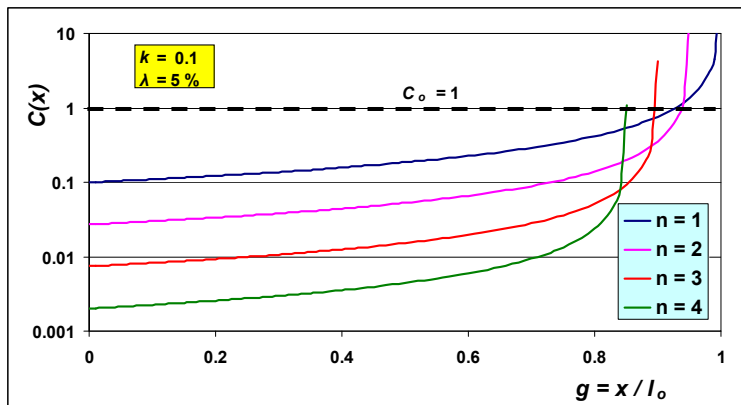
Fig. 5.4 Concentration profiles of directional crystallization for different values of the distribution coefficient  $k$

In refining by directional crystallization special attention is given to important admixtures whose distribution coefficient is lower than 1. In this case, the movement of the solidification boundary through the solidifying crystal is accompanied by gradual enrichment of the melt with the admixture with  $k < 1$ , i.e. in the enrichment of the end part of the solidified ingot with the total length  $l_o$ . On the other hand, the beginning of the ingot is depleted in the admixture with  $k < 1$  (Fig. 5.4). The situation is reversed in the case of admixtures with  $k > 1$  which enrich the initial parts of the solidifying ingot and the end part of the ingot is depleted in these admixtures.

However, conventional directional solidification is a **one-off process**. If the ingot with the resultant concentration profile  $C(x)$  is remelted, this results, due to convection flows in the melt, in the equalisation of the concentration of the admixture in the entire volume of the melt to the initial value  $C_o$ . After repeated directional crystallization, the identical concentration profile  $C(x)$  forms along the entire length of the ingot.

In order to ensure efficient directional solidification, the contaminated part of the ingot must be removed. In practice, this is carried out by two methods:

- The first method is based on the sectioning of the solidified ingot, i.e. the removal of the contaminated part. This is followed by the assembling of cleaner sections and several ingots, with subsequent repeated re-melting by directional solidification.
- The second method is based on melting the material in a boat of a special design. This design enables the removal of the enriched fraction  $\lambda$  of the mother melt from the end part of the ingot, Fig. 5.5, which would be last to solidify and which is expected to have a higher concentration of the admixtures with  $k < 1$ . After the removal of the enriched portion  $\lambda$ , the initial level  $C_o$  of the admixture is reduced in the boat to  $C_p$ . If this process is repeated several times, it is the multiple **directional solidification with the removal of material**.



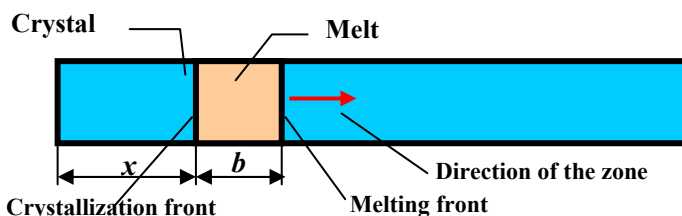
**Fig. 5.5** Concentration profiles of the admixture after the quadruplicate directional crystallization with the removal of material ( $n$  – number of directional crystallization processes)

## 5.2.2 Zone melting

Zone melting is a variant of directional solidification used for the refining of substances to obtain high purity and takes place during the controlled distribution of impurities and admixtures present in the ingot by the periodic repetition of the refining crystallization process in the restricted part, the zone, of the melted ingot, Fig. 5.6.

In zone melting, in an ingot with length  $l_o$  only a defined part is melted, i.e. **a narrow zone**, with the width  $b$ . The molten zone with the concentration of the admixture in the melt  $C_L$ , which travels through the ingot, is characterised by two interfaces between the melt and the solid phase (see Fig. 5.6):

- the melting front ( $x+b$ ), in which the initial solid phase of the concentration  $C_o$  is melted in the zone;
- the solidification front, in the area ( $x$ ), where the material with concentration  $C_L$  melted in the zone and homogenised by convection in the melt, is again solidified, with a new concentration  $C(x)$ .



**Fig. 5.6** Principle of the zone melting



The concentration profile of the distribution of the admixture which gradually formed as a result of the repeated passage of the zone, can be described for the first passage of the zone (Fig. 5.7) of the ingot by the equation derived by Pfann:

$$C(x) = C_o [1 - (1 - k) \exp(-kx/b)] \quad (5.6)$$

where  $C_o$  is the initial concentration of the given admixture in the entire volume of the ingot;

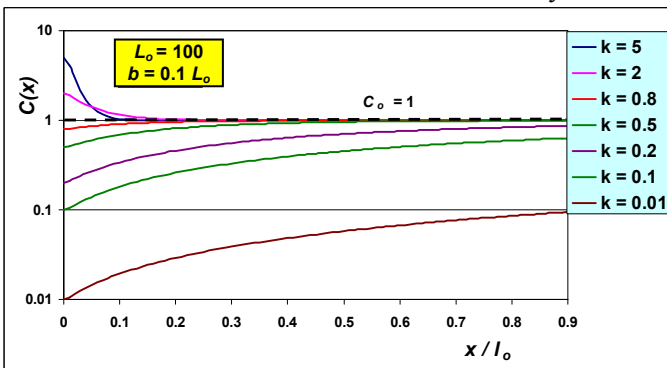
$b$  is the width of the zone;

$C(x)$  is the new concentration of the admixture in the solidified part of the ingot in the area  $x$  after the single passage of the zone. In the case with  $x = 0$ ,  $C(x = 0) = C(0) = k C_o$ .

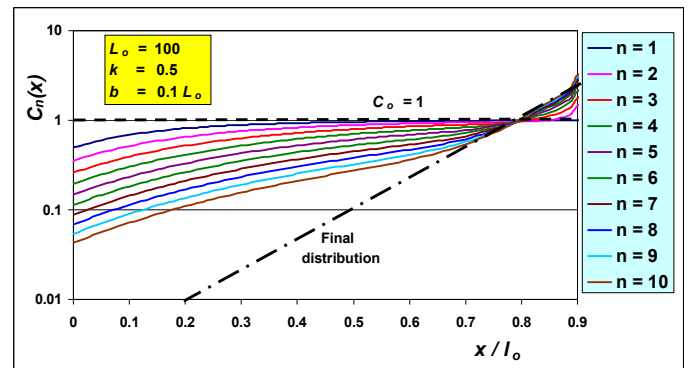
For multiple zone melting, on the basis of the law of the conservation of mass, it was possible to derive an equation for calculating the concentration in the crystal after the  $n$ -th passage of the zone. The equation (5.7) defines the relationship between the change of the concentration of the admixture in the advancing zone and the difference between the flow of the admixture arriving in the zone and the flow of the admixture leaving the zone. The equation was derived using the following simplifying assumptions: the width of the zone  $b$  does not change, the cross section of the zone is constant,  $k$  is constant, there is no change of the volume during solidification, mixing of the melt is perfect and there is no diffusion in the solid phase. The final equation has the following form:

$$C_n(x) = \frac{k}{b} \left[ \int_0^{x+b} C_{n-1}(x) dx - \int_0^x C_n(x) dx \right] \quad (5.7)$$

but is not valid for the entire length of the ingot. When the melting front of the zone reaches the end of the ingot, this final residue of the melt is characterised by directional solidification.



**Fig. 5.7** Concentration profiles of zone melting after a single passage of the zone for different values of the distribution coefficients  $k$ .



**Fig. 5.8** Concentration profiles for zone melting after 1–10 passages of the zone including final distribution

The comparison of the concentration profiles of zone melting and directional solidification for  $k < 1$  indicates (see Fig. 5.5 and Fig. 5.7) that the degree of depletion in the admixture in the narrow zone in zone refining is, as a result of the smaller volume of the zone, lower in comparison with the mother liquid can spread widely along the entire length during directional solidification. Consequently, after the single passage of the zone, the level of the concentration of the foreign admixtures in the ingot subjected to a single zone of the melting is higher in comparison with directional solidification.

Figure 5.8 shows the increase of the refining effect after 1–10 passages of the zone. Comparison with directional solidification and its concentration profile indicates that zone melting is an efficient method of refining only if the process is carried out as a multiple refining process. Depending on the parameters of  $b$ ,  $k$  and  $l_o$ , it is possible to obtain the final or limiting distribution.

A shortcoming of zone melting and also directional solidification when used as the refining method is the joint presence of the impurities with  $k > 1$  and  $k < 1$  in the main substances. Therefore, prior to selecting these refining methods, it is necessary to evaluate the presence of all impurities in the main substance and their possible distribution in relation to the values of the distribution coefficients or select a different method of removal of these impurities.

A greater effect may be obtained by the so-called **zone refining with the removal of material** in which the final small part of the zone refined substances is gradually removed, for example, after every pass of the zone, from the end of the ingot (at  $k < 1$ ). This process is characterised by the highest degree of enrichment with admixtures, yield of refined material. Zone melting is used, in addition to the production of high purity substances, also for the preparation of micro-alloyed parts of the zone refined ingot or for growing single crystals of high purity substances (silicon, germanium, refractory metals, etc.).

## **5.3 CRYSTALLIZATION METHODS OF REFINING AND PRODUCTION OF SINGLE CRYSTALS OF METALS, ALLOYS AND SPECIAL MATERIALS**

### **5.3.1 General classification**

There are more than 100 technologies used for refining different materials, for the preparation of crystals of metals, non-metals, their compounds and alloys with the required content of alloying elements. Crystalline and amorphous substances can be prepared from the gas, liquid or solid phase. Crystallization from the melt is usually preferred due to a very large number of advantages because this method can be used to produce large crystals defined by their external shape, dimensions, the degree of chemical purity and structural perfection. In the majority of cases, the crystals are used directly as the initial materials for further technological processing (for example, production of integrated circuits, electrical engineering, electronic or optoelectronic elements). The crystallization methods, based on the principles of directional solidification and zone melting, are used in production for the refining of the main substances to the maximum possible purity and for the production of crystals with the homogeneous or given distribution of the admixtures.

When designing equipment for refining of substances by the crystallization methods, it is therefore necessary to propose the optimum parameters which affect the degree of separation of the admixture and the time required for obtaining this degree, selecting a more suitable shape of the solidification vessel, the method of heating and cooling, and the mechanism of the process. For example, in refining by zone melting, to obtain the required yield of the material of the given purity in the shortest possible time and with the minimum expenditure, it is necessary to select the number of passages of the zone  $n$ , the length of the zone  $b$ , the distance between the zones, the speed of movement of the zone  $v$  and the method of stirring the melt. The small length of the zone and the small distance between the zones reduce the time required for individual passages. As a result of an increase of the speed of movement of the zone, the effective distribution coefficient  $k_{ef}$  in the macro-space of the ingot approaches 1 and, consequently, the efficiency of the process decreases.

When selecting refining methods, it is therefore necessary to select the shape and dimensions of the solidification mould, the heating method, the arrangement of the process, the displacement mechanism, the method of mixing the melt, and the suitable atmosphere or vacuum.

### **Classification of the methods of refining and production of crystals:**

- a) ***On the basis of the position of the solidification mould or crystal***
  - horizontal (Fig. 5.9 b, d),
  - vertical (Fig. 5.9 a, c, e, f).
- b) ***According to the size of the volume of the molten charge***
  - directional crystallization – the Bridgman method (Fig. 5.9a)
    - the Czochralski method (Fig. 5.9c)
  - the zone melting
    - in a solidification mould (Fig. 5.9d)
    - the floating zone (FZ) method (Fig. 5.9e)
- c) ***According to the atmosphere used***
  - vacuum
  - inert atmosphere (He, Ne, Ar, N<sub>2</sub>)
  - reaction atmosphere (H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CO, S<sub>2</sub>, As<sub>2</sub>, Cl<sub>2</sub>, I<sub>2</sub>)
- d) ***According to the pressure in the melting chamber***
  - a very low pressure (a high vacuum)
  - reduced pressure
  - atmospheric pressure
  - high-pressure (melting in an autoclave)
- e) ***According to the material of the solidification mould (in order to prevent contamination of the crystal)***
  - the crucible-less method (FZ) (Fig. 5.9 e)
  - the auto-crucible (the crucible is made from the same material as the crystal (Fig. 5.9 f)
  - oxide materials (quartz, Al<sub>2</sub>O<sub>3</sub> - corundum, MgO, CaO, ZrO<sub>2</sub> ...)
  - graphite (for materials which do not form carbides)
  - copper (copper-plated, water-cooled boat or solidification mould)

- boron nitride (for semiconductor materials)
- noble metals (platinum, iridium) for reactive and oxide materials

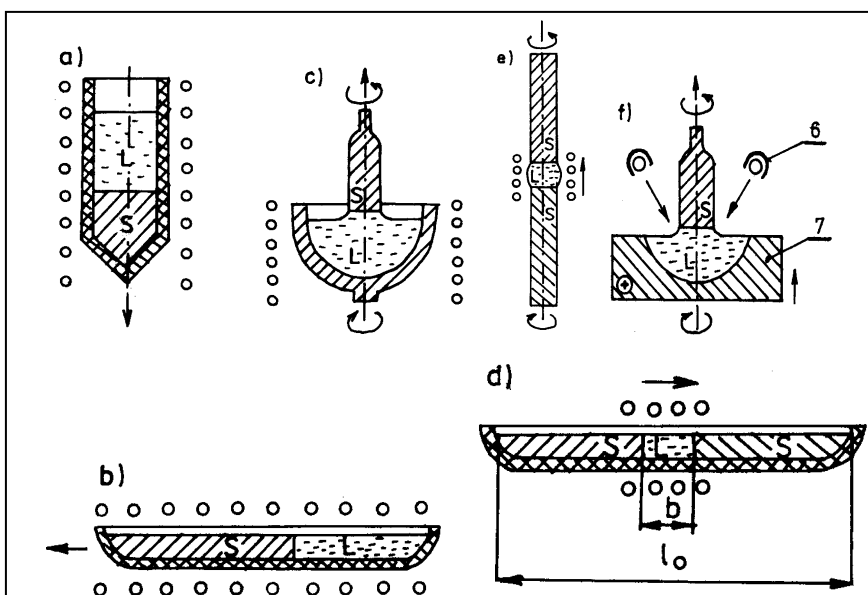
f) **According to the heating method**

- resistance heating
- induction (high frequency and low frequency heating)
- gas heating
- electric arc heating
- plasma heating (low-temperature plasma, high-frequency plasma)
- electron beam heating (the beam of accelerated electrons)
- ion heating (ion beam)
- heating by radiation (solar furnaces, laser)
- freezing-out (liquid CO<sub>2</sub>).

g) **According to the mixing method**

- the rotation of the crucible and the crystal
- induced high frequency current
- mechanical
- magnetic, electromagnetic.

Below, we present a brief review of several selected methods of refining and preparation of single crystals.



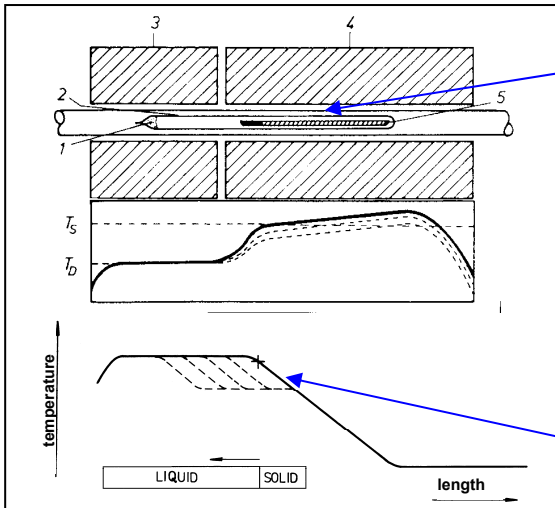
**Fig. 5.9** Methods of refining and production of crystals from the melt

- a) Bridgman – Stockbarger method
- b) Directional crystallization (horizontal arrangement)
- c) Czochralski method (CZ)
- d) Zone melting (horizontal arrangement)
- e) Crucibleless zone melting, i.e. the floating zone method (FZ)
- f) CZ method – melting in the auto-crucible

### 5.3.2 Bridgman method

The Bridgman method is one of the simplest methods and, consequently, is used widely. It is available in the horizontal or vertical arrangement. Figure 5.9 a) shows the vertical arrangement with a seed in the lower part, referred to as the Bridgman–Stockbarger method. The vessel (crucible) with the charge and the seed in the lower part is placed in the heating zone of the furnace. During slow passage of the crucible (or boat) with molten metal through a steep temperature gradient, gradual directional solidification of the melt and, consequently, growth of the crystal takes place. There are three main types of the arrangement:

- The crucible moves in a stationary furnace from the region of temperatures required for melting of the metal into the region of the crystallization temperature of the metal.
- The moving furnace moves through the rigidly secured crucible (boat); this is efficient in particular for operation in vacuum.
- The furnace and the crucible with the melt do not move. Gradual directional crystallization is achieved by a controlled decrease of the temperature of the furnace (the method of the „Horizontal Gradient Freezing” or the method of „Electro-Dynamic Gradient Freezing”) – Fig. 5.10.



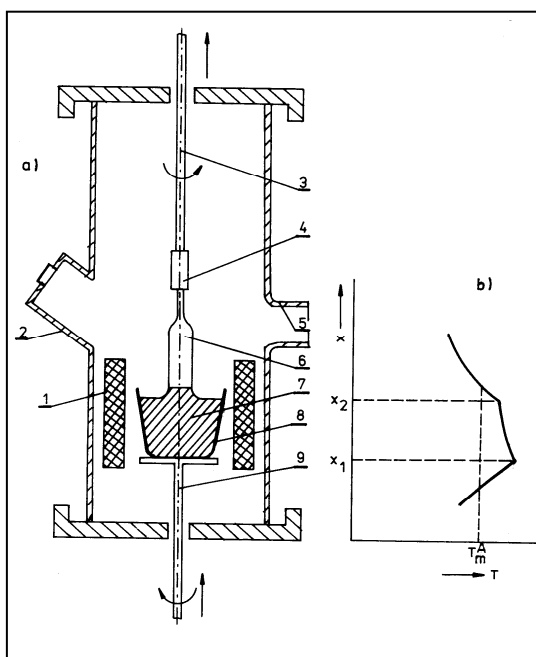
**Fig. 5.10 a)** "Horizontal Gradient Freezing" method  
 1 – reservoir with easy volatile substance (arsenic)  
 2 – quartz ampoule  
 3 – low-temperature resistance furnace  
 4 – high-temperature resistance furnace  
 5 – boat with the melt of semiconductor compound GaAs  
 $T_S$  – solidification (crystallization) temperature of the compound  
 $T_D$  – dissociation (vaporization) temperature of the volatile substance (As)  
 Time flow of temperature changes is drawn in dashed line.

**Fig. 5.10 b)** "Electro-Dynamic Gradient Freezing" method

### 5.3.3 Drawing the crystal from the melt - Czochralski method of single crystal preparation

The method is based on a procedure in which a seed crystal is immersed in the melt in the crucible, the seed is partially melted and, subsequently, is withdrawn from the melt at a lower rate, Figs. 5.9 c) and 5.11. The temperature distribution in the cross-section of the crystal must be symmetric in relation to the axis of the crystal; this is supported either by the rotation of the seed or rotation of the crucible with the melt, or rotation of both. The rotation of the crystal and the melt ensures sufficiently high homogeneity of the melt and the minimum width of the diffusion layer at the solidification front. The crucible with the melt is placed inside the closed space of the furnace in vacuum or an inert atmosphere to prevent oxidation of the melt. The heating source is represented by resistance or induction heating. The usual drawing rate is  $1 \cdot 10^{-4} - 1 \cdot 10^{-3} \text{ cm} \cdot \text{s}^{-1}$  at a rotation speed of 0.1 to  $1 \text{ s}^{-1}$ . The temperature of the melt in the crucible should be maintained at required value slightly above the melting point of the given metal with a relatively high accuracy of  $\pm 1 \text{ K}$ .

The temperature distribution along the axis of the crucible in the **Czochralski solidification equipment** is shown schematically in Fig. 5.11 b). The isotherm, corresponding to the solidification temperature of the substance, is situated above the surface of the melt. The temperature in the crucible increases in the direction to the bottom of the crucible. The single crystal seed and the growing crystal are used for the efficient removal of heat from the solidification front. The form of the surface of the melt is affected by gravitation and the surface tension of the melt. The rate of withdrawal of the crystal, the speed of rotation and the temperature of the melt in the crucible also affect the shape of the crystal–melt phase boundary. At a high temperature of the melt or a high withdrawal speed, the solidification isotherm is situated above the surface of the melt resulting in a decrease of the diameter of the crystal. On the other hand, a decrease of the temperature of the melt and the speed of withdrawal increases the diameter of the crystal which is utilised in practice.



**Fig. 5.11** The equipment for the Czochralski method of drawing single crystals from the melt.

- a) Section through melting equipment,  
 b) Temperature distribution in the axis of the crucible,

- 1) electric resistance heater, 2) inspection window, 3) drawing bar, 4) seed holder, 5) connection of vacuum system, 6) single crystal, 7) melt, 8) silica crucible, 9) crucible holder.

The Czochralski solidification method can be used for producing large single crystals from the melt (in the case of silicon, the diameter to 30 cm, length up to 200 cm) and also the required geometrical shape. The preparation of dislocation-free single crystals of silicon is carried out using the so-called **Dash method** (formation of a neck) when the annihilation of dislocations from the seed takes place in the narrow part between the seed and the actual crystal. The preparation of dislocation-free crystals or crystals with a low dislocation density should be carried out using the initial material with high chemical purity, a perfect seed, a low growth rate, a small axial temperature gradient, a flat phase boundary, and a minimum temperature gradient in the radial direction. The advantage of the method is that the growth conditions can be controlled quite easily, regulated and also automated. The crystal grows in the free space so that there are no problems with contamination and difficulties associated with the growth of single crystals in the crucible or boat (formation of mechanical stresses in the crystal during solidification and cooling, difficult handling of the crystal, etc). The concentration profile of the admixtures along length of the crystal is identical with the concentration profile in directional solidification. The crystals prepared by the Czochralski method are, however, often characterised by a layered structure, i.e. transverse growth chemical inhomogeneity, resulting from the fluctuation of the temperature of the melt at the phase boundary caused by the problems with temperature regulators or uplift convection.

### Liquid Encapsulated Czochralski (LEC) method with covering melt

Czochralski drawing equipments can also work with the overpressure 6 to 20 MPa. These furnaces are used for the preparation of semiconductor compounds single crystals with high pressure of vapors of components (As, P) at the melting temperature of GaP, GaAs.

Evaporation of melted and volatile elements is prevented also thanks to covering of the melt with the substance which does not react with the material used for crystal drawing. **Liquid encapsulation** on the melt prevents escape of volatile components as well as protects the melt from contamination of surroundings.  $B_2O_3$ , CaO, CaCl<sub>2</sub>, BaCl<sub>2</sub>, KCl... are suitable materials for this. LEC method is used for growth of single crystals GaAs, GaP, HgTe...

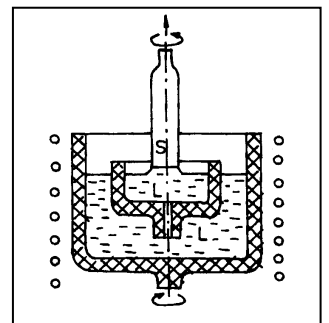
### Preparation of single crystals with a homogeneous or given distribution of admixtures

Single crystals with the homogeneous distribution of admixtures or alloying elements in the axial direction in the macro-volume of the ingot in the directional solidification can be obtained basically by two methods based on:

- Maintaining a constant concentration of the admixture in the vicinity of the solidification front under the condition  $k_{ef} = \text{const}$ .
- Programmable change of  $k_{ef}$  in the process of single crystal growth.

In the first method, the constant content of an element in the melt can be ensured by external supply from the solid, liquid or gas phase, by means of the composition calculated in advance. The floating crucible method is used in the Czochralski method (Fig. 5.12) on the basis of the procedure in which the constant concentration of the elements in the internal vessel, in which solidification takes place, is ensured as a result of constant supply of the melt from the external crucible. The concentration of the admixture in the external and internal crucibles and the ratio of their dimensions are determined by the value of  $k_{ef}$ . This makes it possible to obtain the constant concentration of the admixture along the entire length of the crystal. A similar procedure can be used in homogenising in zone melting (the method of the starting charge).

The second method is based on the Burton–Prim–Slichter equation (5.3), according to which the value of  $k_{ef}$  can be affected by the change of the solidification rate and the speed of rotation of the crystal and the crucible, i.e. forced convection in the melt. Selection of the programme for obtaining a homogeneously alloyed crystal in the axial direction is based on the determination of the dependence of the rate of solidification and rotation speed on the drawing time or the length of the crystal. This method can be efficiently combined with the floating crucible method where by selecting the suitable form of the internal crucible it is possible to produce single crystals with a programmed distribution of elements. A similar procedure is used for the preparation of oriented dendritic ribbons of semiconductors produced by rapid withdrawal from the melt.



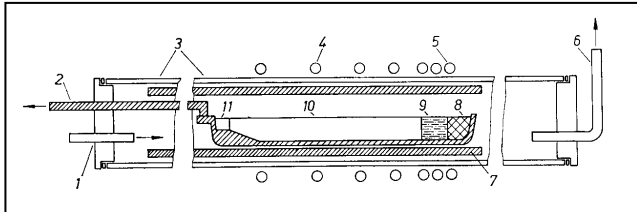
**Obr. 5.12** The floating crucible method

## 5.3.4 Zone melting methods

### Horizontal zone melting

Equipment for refining of metals by horizontal zone melting in a boat consists of three sections: a boat with a charge, a heating source capable of forming a narrow molten zone in the charge, and a mechanism for moving the boat or the heating source – Fig. 5.13. The material of the boat and the atmosphere of this furnace must not contaminate molten metal. In single crystal production, an oriented seed is placed in the boat and it is necessary to maintain the constant length of the zone during the entire passage or, in some cases, repeated passages of the zone through the specimens. In order to maintain the constant length of the zone, there should be a steep temperature gradient at both ends of the molten zone.

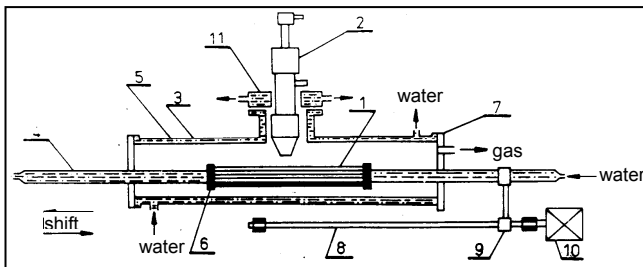
The heating source include resistance heating, high frequency induced current, electric arc, electron beam accelerated by the electric field, the flux of photons (laser), focused solar energy (solar heating), etc. The zone melting of refractory metals is carried out in most cases by electron or plasma heating resulting in higher temperatures and enabling efficient control of the process. Induction heating is the most suitable method for metals with medium melting points. Homogeneity of the melt can be ensured by electromagnetic stirring.



**Fig. 5.13** Device for horizontal zone melting and preparation of germanium single crystals

1 - gas inlet (Ar, Ar + H<sub>2</sub>), 2 - shift holder, 3 - quartz tube, 4, 5 - inductors (coil), 6 - outlet gas, 7 - graphite tube, 8 - polycrystalline Ge bar, 9 - remelted zone, 10 - Ge single crystal, 11 - seed.

**Plasma heating** is used in the production of special alloys and, in particular, in the metallurgy of high-purity alloys. Plasma forms as a result of thermal ionisation of the gases – argon, nitrogen, hydrogen and other inert gases in the electric arc. Generators of low-temperature plasma include plasma torches working with the electric arc concentrated by a nozzle with the joint aerodynamic effect of the flowing gases. The VŠB-TU of Ostrava (Czech Republic) developed a plasma torch with the continuous stabilisation of the electric arc running between a water-cooled cathode produced from thoriated tungsten and a copper nozzle used as an anode. Other types of plasma torch (plasmatoms) are based on the **ionisation of gas** in the high frequency field operating with frequencies of up to several tens of MHz.



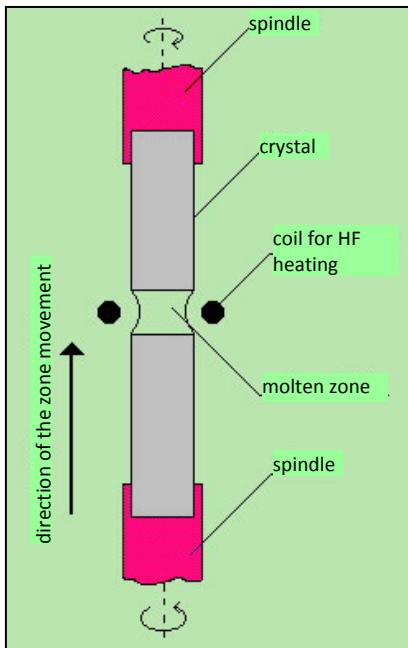
**Fig. 5.14** The equipment for plasma melting of metals

1) solidification mould, 2) plasma torch, 3) external jacket, 4) carrier pipe, 5) internal jacket, 6) front end of the solidification mould, 7) furnace flange, 8) guide screw, 9) carrier, 10) electric drive, 11) cooler.

The Department of Non-ferrous Metals, Refining and Recycling of the VSB-TU of Ostrava developed, for special applications in the preparation of high purity metals by zone melting, a plasma furnace with a horizontal, copper, water-cooled solidification mould operating with a low-temperature plasma torch (Fig. 5.14). The furnace can be used for melting metals with medium melting points (Fe, Co, Ni) and with high melting points (Ti to Mo), and for special high-alloyed alloys (Fe-N, Ni-Ti, Al-Fe-Mo, etc.) which cannot be often prepared by other methods because of the high volatility of components (Cr). This furnace operates with a slight excess pressure of the atmosphere of the ionised gas or a mixture of gases (Ar, Ar-N<sub>2</sub>, Ar-H<sub>2</sub>) and produces temperatures of up to 10000 K in the plasma arc.

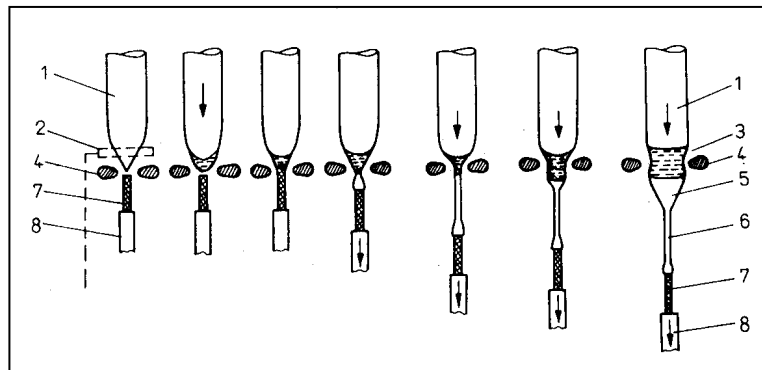
Plasma heating is used on an increasing scale for the intensification of metallurgical processes, for the refining of metals and preparation of single crystals of refractory metals, alloys and compounds. The plasma-forming gas also ensures additional refining of metals by the reactions  $Ar^+ + e^-$  with the melt, the reaction of oxygen and hydrogen in plasma with admixture elements in the melt, and the removal of volatile substances from the superheated melt.

## Vertical zone melting – FZ method



**Fig. 5.15** Principle of the FZ method

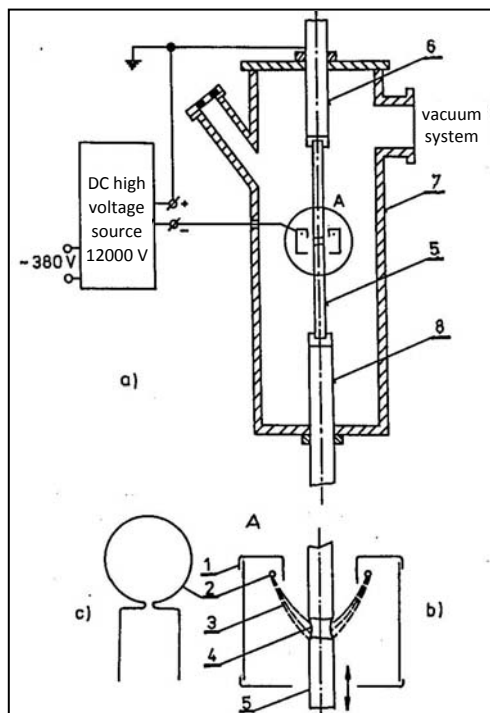
Crucible-less zone melting, i.e. the **floating zone method (FZ)**, Fig. 5.15, is one of the most efficient and widely used methods of refining and preparation of crystals of reactive substances and refractory metals. The narrow molten zone is produced by, for example, high frequency, electron beam, laser and solar heating.



**Fig. 5.16** Progress at the production of silicon single crystals in using of the zone melting with HF induction heating (FZ method)

1 - polycrystalline rod, 2 - graphitic susceptor, 3 - zone, 4 - inductor, 5 - growing single crystal, 6 - neck (Dash necking), 7 - seed, 8 - seed holder

Electron beam zone melting (Fig. 5.17) in high vacuum using suitably oriented nuclei (seeds) can be used for the preparation of single crystals of refractory metals: W, Mo, Ta, Nb, V, Zr, Ti, Re. The zone is maintained in the suspended state mainly by surface tension forces. The stability of the zone depends on gravitation, surface tension and density of the melt, the concentration of the admixtures and the direction of movement of the zone. The stability of the zone is maintained using an external magnetic field with the so-called support frequency.



**Fig. 5.17** Equipment for electron beam zone melting in vacuum by the floating zone method.

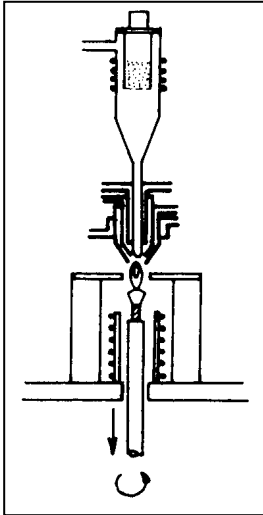
- a) section through melting equipment,
- b) section through focusing system,
- c) the shape of the tungsten cathode.

- 1) focusing system consisting of Mo sheets,
- 2) cathode (tungsten wire  $\varnothing$  0.5 mm),
- 3) electron beam,
- 4) molten zone,
- 5) metal used for melting,
- 6) upper holder of the bar,
- 7) the jacket of the recipient,
- 8) lower holder of the bar.

In electron beam zone melting, in addition to the effect of zone refining, a significant role is played by secondary processes. They cause the generation of gases and evaporation of admixtures with a high vapour tension in the conditions of working vacuum of  $10^{-3} - 10^{-6}$  Pa. The single crystals of metals, produced by this method, are not perfect, especially when the bar diameter is large. During the growth of the crystal and its solidification, samples contain a steep temperature gradient, the crystal–melt interface is curved and, consequently, mechanical stresses form in the crystal. Nevertheless, this method has been used for the growth of single crystals of W, Mo, Ta and Nb with large, slightly disoriented subgrains and with the dislocation density of less than  $10^4 \text{ cm}^{-2}$  inside the subgrains.

## 5.3.5 Special crystallization technologies

### Verneuil method



This method (Fig. 5.17) belongs in the group of the oldest solidification methods for the preparation of single crystals of oxides, in particular ruby, sapphire, etc. It is still used extensively in industry. A charge in the form of a fine powder is placed in a hopper with a vibration feeder situated above the upper part of a plasma torch. The hopper is connected through a funnel with the system of nozzles of an oxygen–hydrogen torch. The powder is regularly discharged through the axis of the nozzle. As a result of heating by the flame, the powder melts and falls on the seed heated by the flame. The rotational and translational movement of the holder of the seed ensures the required growth rate of the single crystal. The surrounding furnace is used for gradual cooling of the grown single crystal.

The selection of materials is limited mainly to oxide materials, in particular of ceramic nature. Despite improvements, the limit of the structural perfection of produced single crystals is lower than, in, for example, the method based on photon heating. This heating is based on the focusing the beam of a high-power light source (plasma torch or sun) to the solidification space.

Fig. 5.18 Verneuil method for the preparation of single crystals of oxides

### Preparation of single crystals from the gas phase, the vapour–liquid–solid (VLS) method

A droplet of a solvent is placed on a crystal substrate and at the given temperature the droplet is additionally saturated by means of a chemical transport reaction, resulting in the formation of a supersaturated solution. The resultant concentration gradient leads to diffusion in the droplet and to crystallization on the substrate. The result is the growth of a sharp-tip ‘whisker single crystal’, with the tip of the crystal covered by the solvent.

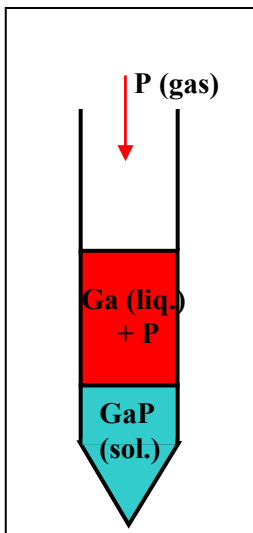
The first stage of growth of this crystal is the formation of nuclei. In the preparation of crystals from the gas phase, the condition for the growth of nuclei is the essential super-saturation of the vapours. According to the current views regarding crystal growth mechanisms, the bonding of atoms to the crystal takes place on steps formed by a screw dislocation. In this case, the formation of a closely spaced plane is never completed and results in spiral growth of the crystal, i.e. a whisker crystal. Theoretically, a single screw dislocation is sufficient for the growth of a crystal at low super-saturation. Crystallization from the gas phase was used to obtain whisker crystals of Ge, Si, Fe, Sn, Zn, Ag, Cu, Ni, etc, with the mechanical strength close to the theoretical value.

The single crystals of refractory metals with a low vapour tension are efficiently produced from the gas phase of their volatile compounds. This is carried out by chemical transport reactions of compounds in the gas phase on the surface of the crystal substrate. This method has also been used to produce, for example, single crystals of W, Mo, Nb, Ta and other refractory metals. The initial materials are halides of these metals, for example, chlorides or fluorides. In this method, the chloride or fluoride of the appropriate refractory metal is placed in the evacuated space and heated to transfer it to the gas phase. Using a hydrogen flow, the vapours of tungsten hexachloride  $WCl_6$  are supplied to the heated tungsten fibre (approximately 1000 °C) where  $WCl_6$  is reduced. The reduced tungsten settles on the heated fibre. When selecting suitable cooling rates, temperature and concentration conditions, a single crystal grows on the seed. As a result of the combined reduction of the mixtures of chlorides, it was possible to obtain alloys of the type W–Mo, Mo–Nb, W–Nb and superconducting layers of  $Nb_3Sn$  on a metallic substrate.

### SSD (Synthesis – Solution – Diffusion) method

Synthesis – Solution – Diffusion (SSD) method is used very often for synthesis and preparation of semiconductor compounds crystals. Classical case is the production of single crystals of stoichiometric compound gallium phosphide (GaP) for laser LED diodes. Principle of the SSD method – see Fig. 5.19. The saturated solution of phosphorus in the gallium melt occurs in the crucible inside the closed ampoule. The bottom part of the crucible has crystallization temperature, the top part is situated at higher temperature. In this way it is possible to ensure the saturation of the melt with phosphorus vapors from outer reservoir with pure phosphorus located in the condensation zone. Crystallization proceeds this way: Phosphorus reacts with Ga excess on the surface of the melt and dissolves in it (Solution), because the higher temperature is here. Phosphorus further diffuses to the bottom of the crucible (Diffusion), in this way it creates necessary super-saturation and occurs the crystallization under





production of GaP (Synthesis) – see Fig. 5.19. Thanks to ampoule movement with suitable crystallization rate it is possible to ensure the isothermal crystallization.

Fig. 5.19 Principle of the SSD method

## Preparation of single crystals from the solid phase – recrystallization methods

The physical principle of crystallization is based on overcoming atomic bonds in the deformed crystal lattice, the formation of nuclei of new grains and subsequent growth by the transfer of atoms from the disrupted areas to thermodynamically more stable positions as a result of the formation of relatively perfect crystals. Recrystallization is accompanied by a decrease of internal stresses. The rate of grain growth depends directly on the initial purity of metal. The grain size after recrystallization annealing depends greatly on the degree of prior plastic deformation. The maximum growth of the grains is recorded at low, so-called **critical degrees of deformation** (2 – 10 %), and also at deformations higher than

90 %.

The recrystallization methods of preparation of single crystals in the form of fibres, wires and ribbons can be divided into:

- the methods utilising the **polymorphous transformation** of the metal in the solid state Fe, U, Ti, Zr, lanthanides;
- the methods of recrystallization annealing of metals after the critical degree (5 – 10 %) of **plastic deformation** (aluminum, tungsten) or after 80 – 95 % deformation (molybdenum, titanium...);
- the methods of **secondary recrystallization** utilising the rapid growth of crystal grains at a specific temperature gradient after alloying with suitable high-melting finely dispersed particles (for example, ThO<sub>2</sub> in W...), thus preventing the growth of further parasitic grains.

## Rapid solidification

During cooling from a melt, metals and alloys solidify at the melting (liquid) temperature. However, as soon as the cooling rate exceeds  $10^{10} \text{ K}\cdot\text{s}^{-1}$ , the mobility of the atoms is theoretically restricted in such a manner that they solidify by the amorphous mechanism, i.e. retain the atomic structure of the melt. At present, it is possible to obtain cooling rates of  $10^6 - 10^8 \text{ K}\cdot\text{s}^{-1}$  and, consequently, the amorphous state can be produced only in certain metallic systems, for example:

|                    |  |
|--------------------|--|
| metal – metalloid: | $\text{Fe}_{80}\text{P}_{13}\text{C}_7, \text{Au}_{81}\text{Si}_{19},$ |
| metal – metal:     | $\text{Cu}_{60}\text{Zr}_{40}, \text{Ni}_{60}\text{Nb}_{40}.$          |

In rapid solidification, a melt jet is sprayed between two rapidly rotating cooled copper rolls. In this case, the amorphous (microcrystalline) solid metallic ribbon with a thickness of several millimetres and several centimetres wide solidifies between the rolls during several microseconds. In fact, the ribbon is injected into the space behind the rolls. In this case, coiling is the technical problem.

**Amorphous metals**, the so-called **metallic glasses**, formed during rapid solidification, are homogeneous materials without grain boundaries and are characterised by high strength and elasticity. In contrast to commercial glasses, they can be compressed by up to 50 %. They are characterised by high corrosion resistance, electrical connectivity and can be easily magnetised and, taking into account low electric losses, they already replace conventional transformer sheets. In heating to temperatures higher than recrystallization temperature, amorphous materials may change to the crystalline state and, consequently, it is important to consider the stability of metallic glasses. The results of these rapid solidification technologies (in addition to metallic glasses) are also structural variants of microcrystalline materials with the grain size smaller than 1  $\mu\text{m}$ .

The processes of rapid solidification are used at present for processing not only magnetically soft materials but also for modification of, for example, the properties of aluminium alloys based on super-duralumin Al–4.5Cu with 1 – 3 % Li. In the case of aluminium it is also possible to obtain a higher solubility of iron, nickel and manganese (3 – 8 %), the solubility of chromium, zirconium and cobalt in copper is increased, and in steels it is possible to increase the solubility of carbon, boron, silicon and phosphorus. Similarly, for special applications it is possible to produce improved types of dispersion-hardened materials with a higher concentration of ultrafine precipitates. The processes of rapid solidification also indicate the trends for materials with the application of trace elements and rare earth metals (lanthanides) in promising areas of electrical engineering and microelectronic materials.

## 5.4 EPITAXIAL TECHNOLOGY

### Principle: growth of the thin monocrystalline layer on the substrate

Epitaxial growth makes it possible to prepare:

- the very perfect monocrystalline layers, much superior than e.g. the volume crystals grown from the melt;
- the very thin layers, often only several atomic planes;
- the perfectly (atomic) connected various semiconductor materials that have minimum defects not only in layers, but also on the interface, then applicable hetero-structures.

### Conditions for growth of layers:

- 1) Present of the oversaturated solution or saturated vapors above the surface of the substrate;
- 2) Growing time (depend on required thickness of layers);
- 3) The same type of the lattice of the substrate and layer;
- 4) Minimum difference in parameters of the crystal lattice of the substrate and layer materials (fulfilled at homogenous junction Si – Si).

### Základní rozdělení dle vztahu vrstva – podložka:

1. **Homo-epitaxy** – substrate (S) and layer (L) have the same macro-chemistry (L is micro-alloyed).
2. **Hetero-epitaxy** – substrate (S) and layer (L) have different chemical composition.
3. **Rheo-taxi** – S is liquid (melt), L – solid state.
4. **Grapho-epitaxy (dia-taxi)** – S is amorphous (glass) with the modified surface.

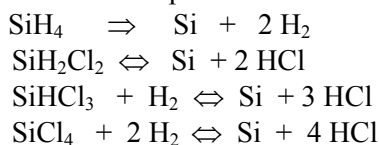
### Základní rozdělení dle technologie:

1. **Vapor phase epitaxy (VPE)** – epitaxy from gas phase, for Si, Ge
2. **Metal-organic vapor phase epitaxy (MOVPE)**
3. **Liquid phase epitaxy (LPE)** – suitable for GaAs, GaP etc.
4. **Solid state epitaxy (SSE)**
5. **Laser epitaxy (LE)**
6. **Molecular beam epitaxy (MBE)**

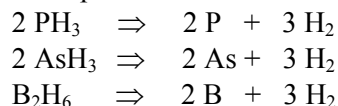
### 5.4.1 Vapor Phase Epitaxy (VPE)

Epitaxial growth is a spreading or deposition process for creation of monocrystalline layers on the single-crystal Si wafers at the temperature around 1200 °C. Si epitaxial layers are used in all bipolar integrated circuits (IC). Various textures are created on Si wafers, i.e. semiconductor devices – transistors, diodes, and also the passive devices – resistors, capacitors, tracking paths, etc. The thickness of Si epitaxial layers can be at intervals 5 ÷ 15 μm, electric resistivity 1 ÷ 5 Ω·cm. Conductivity type can be identical or opposite than the conductivity of Si wafer.

Si epitaxial layers are produced entirely by using of the chemical deposition from gaseous phase, i.e. **Chemical Vapor Deposition** - **CVD** method. The initial reaction components are: silicon tetrachloride SiCl<sub>4</sub>, trichlor-silane SiHCl<sub>3</sub> or silane SiH<sub>4</sub> and hydrogen H<sub>2</sub>. As dopant are used: phosphane PH<sub>3</sub>, arsine AsH<sub>3</sub>, di-borane B<sub>2</sub>H<sub>6</sub>. Chemical reactions proceed at the temperatures 950 to 1200 °C according to kind of the reagent containing Si:



Dopant compounds are extended too:



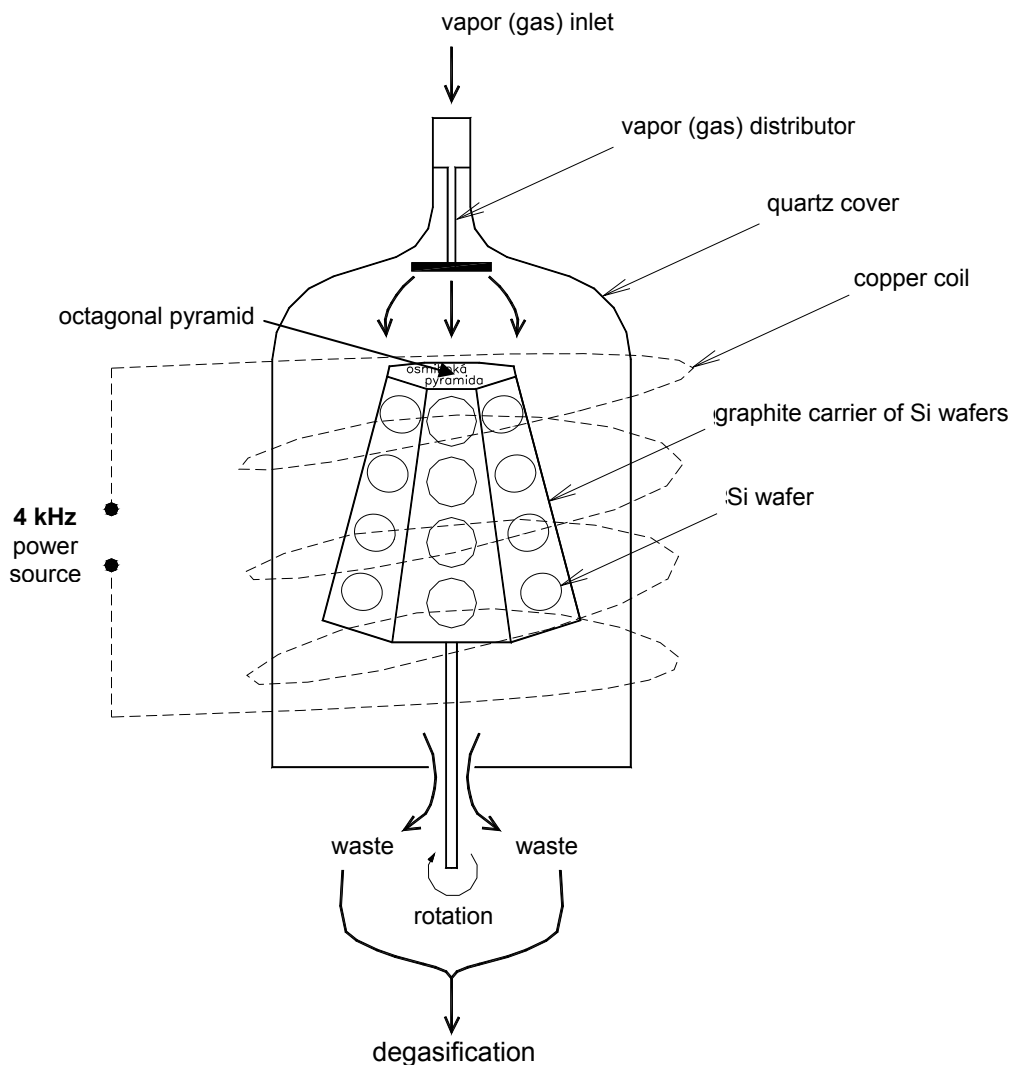
### Properties of reaction substances:

**SILICON TETRACHLORIDE** – fire-resistant fluid, boiling temperature is 57 °C. It decomposes boisterously with water at the creation of SiO<sub>2</sub> and HCl. Incurred moist hydrogen chloride HCl is very corrosive. SiCl<sub>4</sub> is preserved in the stainless containers. From the point of view the electrically active impurities must be purity of SiCl<sub>4</sub> very high. Specific electric resistance of Si epitaxial layers prepared without dotation of the phosphane is about 500 Ω·cm. SiCl<sub>4</sub> is vaporized into epitaxial equipment through bubbling of hydrogen.

**HYDROGEN** is flammable and explosive gas. Explosion limit by air is  $4 \div 74$  vol. % of  $H_2$ . Hydrogen forms the main component of the reaction mixture. It must be therefore extremely pure. Purification of hydrogen is carried out inside the cryogenic cleaner. Its principle is based on the adsorption of impurities on the active carbon at boiling temperature of the liquid nitrogen, i.e. at  $-196$  °C. After the cleaning is total content of impurities lower than  $10^{-5}$  vol. %, i.e. purity of  $H_2$  is better than 99.99999 vol. %.

**PHOSPHANE ( $PH_3$ )** is very toxic gas. It is preserved in the steel compressive bottles diluted with hydrogen on the concentration 0.003 vol. %. Even at this concentration it is very deleterious.

**HYDROGEN CHLORIDE (HCl)** is fire-resistant, very acid gas, which is kept in the liquid state inside of the steel vessels. It is high corrosive.

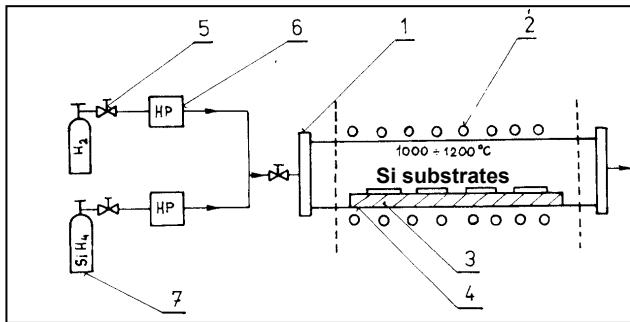


**Fig. 5.20** Equipment for deposition of Si epitaxial layers (coils of the inductor are placed closely beside themselves)

**Silicon epitaxy is technically the best-more exacting chemical process at the technology of the production of micro-chips**

Various types of epitaxial reactors exist. One of the most common types of the modern reactors is the barrel reaction vessel (Fig. 5.20), but also the horizontal reactors with rotating one- or more-plate discs. Reactor is formed with a carrier of Si wafers made from very clean graphite (99.9995 %), coated with the 100  $\mu m$  thick protective layer from silicon carbide SiC (99.9999 %). Graphitic carrier of Si wafers in the form of multi-contest pyramid is placed in a quartz cover. Around the cover is wound a copper coil, which ensures heating of the graphite and then also Si wafers throw inductive currents at frequency of 4000 Hz. Reactive substances flow to the cover from above, i.e.  $H_2$  (flush of the reactor), then  $H_2 + HCl$  (clean-up of the surface of silicon wafers by etching with highly pure gaseous hydrogen chloride),  $H_2 + SiCl_4 + PH_3$  (epitaxial growth),  $H_2$  and in the end inert  $N_2$  (flush of the reactor

and cooling). Waste gases and vapors are sprayed with water, which remove from hydrogen more than 99.9 % of SiCl<sub>4</sub> and HCl. Temperature of Si wafers at the deposition is measured with the pyrometer. Epitaxial growth proceeds at speed around 0.7 μm/min. Hydrogen flow is 300 l/min.



**Fig. 5.21** Horizontal reactor for VPE of Si

- 1 – steel flange
- 2 – HF inductor
- 3 – graphite desk
- 4 – quartz reactor
- 5 – valve
- 6 – flow-meter of gases
- 7 – pressure cylinder

Horizontal reactors with rotating one- or more-plate discs use either radiation heating (bar screens of halogen bulbs are placed above or below quartz reactor) or induction heating – see Fig. 5.21. Their advantage is high homogeneity and high reproducibility of parameters of deposited layers reached especially by construction of injectors of the gaseous mixture, rotation of Si wafers and by using of intensely cooled quartz pipes with small high (small distance between wafers and top wall of the reactor cuts non-homogeneity of the fluxion rising at space above Si wafers owing to natural convection). Disadvantage of these reactors is lower manufacturing capacity.

### **Quality of Si epitaxial layers**

Demands on Si epitaxial layers are very strict:

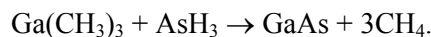
#### **1. Minimum dispersion of resistivity and thickness.**

The lowest dispersion of resistivity and thickness of epitaxial layers is reached at the suitable thermal profile on the graphite carrier of Si wafers and narrowly symmetrical flux of hydrogen with reaction components along graphite carrier.

#### **2) Minimum density of volume and surface defects.**

## **5.4.2 Metal-organic vapor phase epitaxy (MOVPE)**

The gaseous epitaxy from metal-organic compounds is today the most widespread and the most significant method. MOVPE is a technology which gives the similar results as MBE, but makes it possible to prepare the wider spectrum of materials and has essentially higher achievement, suitable even for industrial usage. Its significance depends on the availability of metal-organic compounds with extreme cleanness and on understanding of complicated process production of layers, when play considerable role the chemical reactions at tight proximity of rising layers. Semiconductor substrate is heated inside of the reactor, through that flows the mixture of gases. The largest portion in the mixture has a carrier gas, that's mostly H<sub>2</sub> or N<sub>2</sub>. Molecules containing atoms necessary for epitaxy of required semiconductor are addition into carrier gas. The resulting reaction equation for growth of GaAs layers is:



To achievement of the N-type or P-type epitaxial layers we must super-add to the gas mixture at the epitaxy a slight amount of the other suitable precursors. Silane (SiH<sub>4</sub>) can be used as N-type dopant for GaAs layers. Silicon at the epitaxial growth builds into the crystal lattice on seats of Ga and acts therefore as admixture of N-type. As admixture of P-type we can used the carbon tetrachloride (CCl<sub>4</sub>), that's source of carbon.

## **5.4.3 Liquid phase epitaxy (LPE)**

Double hetero-structures (GaAl)As/GaAs and (GaIn)(AsP)/InP of ternary and quaternary types are the base for the most modern optoelectronic radiation sources, which work in infrared area. Their quality designates effectivity of the electromagnetic energy conversion on optical one, determines static and dynamic parameters of luminescent and laser diodes, the degradation and lifetime of radiation sources and many other parameters. Mastered technology of the preparation of layers requires a high quality of mono-crystalline substrate with minimum dislocation density, with perfect crystal lattice, with suitable orientation and with other electric and optical properties. LPE dominates at the industrial production (largely for preparation of LED diodes) and manages to prepare also quantum holes. It isn't suitable for preparation of the complicated quantum sizable structures or systems with controlled change of composition.

## Principle of the LPE method:

The basic technology for preparation of the double hetero-structure is epitaxial growth from liquid phase. **Liquid epitaxy we can define as a growth of layers on the monocrystalline oriented substrate from the melt.** For it is necessary to prepare at the given temperature a saturated solution of needed material in suitable solvent and make contact of this solution with the substrate usually in graphitic cassette. Growth of the layers is ensured either with the gradual decreasing of the temperature in the system, e.g. reducing of the substrate temperature or super-saturation of the liquid solution (melt).

The suitable solvents for  $A^{III}B^V$  compounds are Ga or In, whose melting temperature is low. To growing of binary compounds is enough in this solution to dissolve the appropriate element from V. group. Temperature is chosen so as to the dissolution was perfect (600 to 900 °C). Elements with higher proton number require usually the lower temperature. Ternary and quaternary semiconductors are prepared in a similar manner, however it is necessary to know the relationship between their composition in solid-state and in liquid phase, i.e. know their equilibrium phase diagram.

At the liquid epitaxy are as dopants used elements that are usually added directly into the solution. The important property is their distributing (segregation) coefficient, which characterizes their ability to pass into the solid phase. Majority dopants have this coefficient low. Therefore happens to their enriching in the solution (melt) and this way can enlarge also their amount in the growing epitaxial layer. Dopants of P-type in GaAs layers can be: Zn, Cd, Mg and Ge, which is amphoteric. Elements Sn, S, Se and Te are dopant of N-type.

## LPE methods:

**A) Non-stationary methods** – during the epitaxial growth is changed the temperature – crystallization is non-isothermal.

1) **Nelson's turn-over method** – see Fig. 5.22. The substrate is placed on the top part of the container, at the bottom finds the saturated solution in melt, on whose surface swims a saturated solid phase. As you can see from Fig. 5.22 a) and from the time path of the temperature - Fig. 5.22 b) the melt is after the turn-over in contact with the substrate and starts the process of the crystallization behind gradual temperature decreasing.

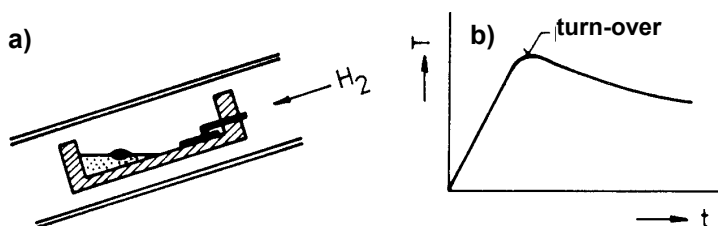


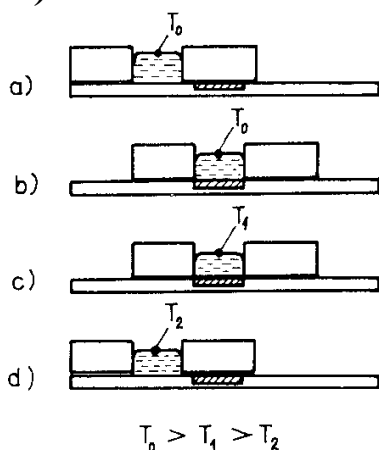
Fig. 5.22 Principle of the Nelson's LPE turn-over method

2) **Rotary variants LPE.** Instead of turn-over process of the bowl is used the rotation of tube.

### 3) Dipping variants LPE

This method is used for the production of magnetic monocrystalline layers on the different kinds of garnets and for preparation of other semiconducting layers. The saturated solution of the melts is found in the crucible (e.g. Ga-Gd-garnet) in  $PbO \cdot B_2O_3$ . First is the solution in melt under-cooled, i.e. is super-saturated and after them the substrate is deep into melt and all system is cooled down.

4) **LPE cassette method** – see Fig. 5.23. In stage a) a cassette with a solution in the melt (e.g. Ga) is found in the



separate space containing material, from which will be crystallize new epitaxial layer. The solution is slightly overheated, i.e. it is in non-saturated state. The substrate is placed outside this space in separate parts of the cassette (slide-valve). Both parts of the cassette are each other movable. After the temperature equalization on  $T_0$  will the slide-valve move the substrate below the melt – stage b). At that a slight melting-down of the substrate takes place thereby to removing the failed surface layer. In stage c) happens the growth of epitaxial layer during reducing temperature on  $T_1$ . Having finished crystallization, i.e. after achievement of needed thickness of layer, the slide-valve moves the substrate into the original position. The whole system is cooled on temperature  $T_2$ .

Fig. 5.23 LPE cassette method

A) **Stationary methods** – crystallization proceeds at the constant temperature. Driving force of the crystallization is a saturation of the melt at constant temperature gradient..

B) **Combined methods** – combination of both above-mentioned methods makes possible the preparation of multiply structures, especially for optoelectronic devices. It's used e.g. for preparation of hetero-structural lasers  $\text{Ga}_{1-x}\text{Al}_x\text{As}/\text{GaAs}$ .

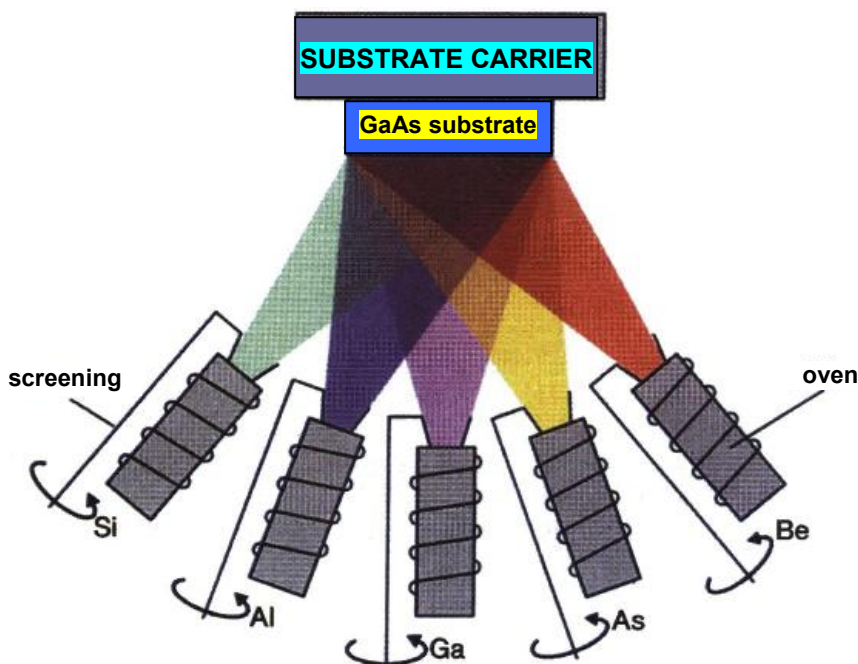
### Application of LPE:

With using the LPE method are prepared the layers especially for semiconductor compounds of  $\text{A}^{\text{III}}\text{B}^{\text{V}}$  or  $\text{A}^{\text{II}}\text{B}^{\text{VI}}$  types on the ground of high volatileness (flightiness) of one or both components at melting temperature of the compound that lies considerably high above the melting temperature or sublimation temperature of basic components. Compound GaP has melting temperature higher than 1500 °C, while gallium only 29.8 °C and phosphorus 44 °C, whereas phosphorus has high tension of vapors at increased temperatures. Method LPE is substitutable also for the production of so-called „bubbly memories“, i.e. memories with cylindrical domains and at most of other optoelectronic devices.

## 5.4.4 Molecular Beam Epitaxy (MBE)

**MBE** is the most perfect variant of vacuum evaporation methods (Fig. 5.24). Growth of type „gas – solid“ proceeds in ultra-high vacuum (**UHV**) behind relatively low temperature with evaporation of molecules, eventually atoms (mono-atomic molecules) which come in the beam on the warmed substrate, where condensate. The substrate surface is atomic pure with minimum roughness. Growth of layers it is possible perfectly to check in atomic scale; growth rate is cca one atomic layers per second ( $< 0.6 \text{ nm/s}$ , i.e. about  $1 \mu\text{m}$  per hour). It is possible to reach the jump concentration changes, atomic flat surfaces and excellent homogeneity of properties on the surface of the whole layer.

The **MBE method** is advisable for the preparation of multiply structures in semiconductors, where individual layers are very thin and differentiate by properties. Their interface must be very sharp and smooth. Controlled growth is possible to prepare layers starting with one atomic layer. The method is based on using of elements in solid-state. Chosen chemical elements, e.g. Ga, As, Al, are heated in high vacuum in electric ovens, called by **effusion cells**. Evaporated atoms or molecules get out of cells in directed beams and limp on heated monocrystalline substrate. They react here together and step by step create monocrystalline layer. Molecular beams can be interrupt by help of screenings before the mouth of individual cells thereby determine the composition and properties of rising layers. Another cells contain elements so-called dopants (e.g. Si and Be), which influence the type of electric conductivity rising semiconductor (N- or P-type in GaAs). Apparatus is further equipped with the electron gun for heating of substrates (0 to 700 °C) and with fluorescent screen for the **Reflection High-Energy Electron Diffraction (RHEED)**. Individual effusion cells, as well as walls of the chamber, are behind running cooled with liquid nitrogen ( $-197 \text{ °C}$ ).



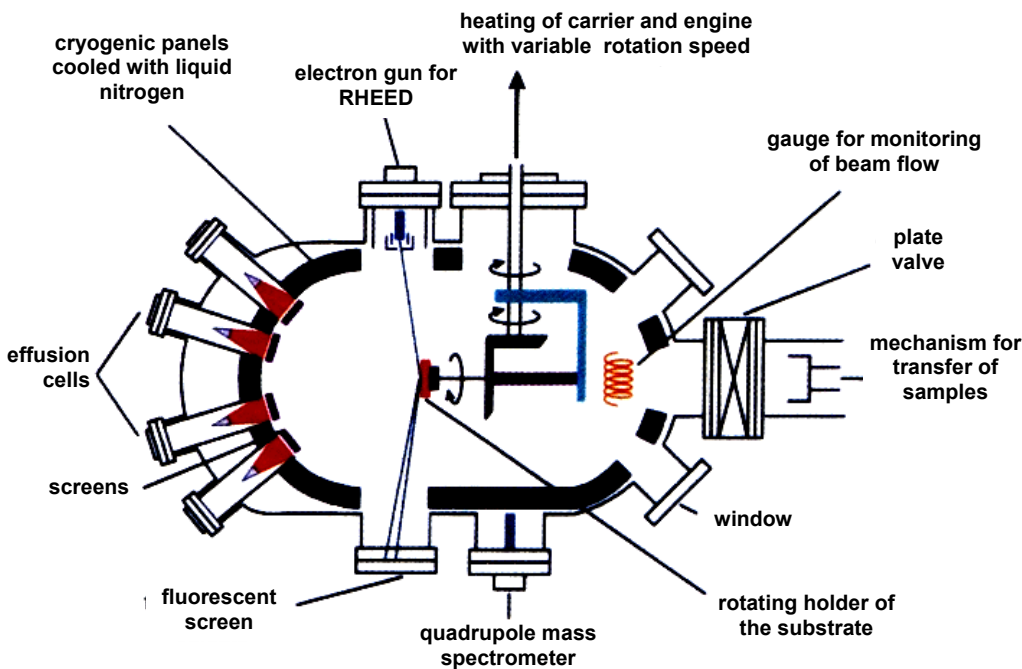
**Fig. 5.24** Scheme of the MBE process at the growth of epitaxial layers on the GaAs substrate

Typical working temperatures in effusion cells: Ga 1000, As 300, Si 1100, Al 1200, Be 900, substrate 550 [°C]

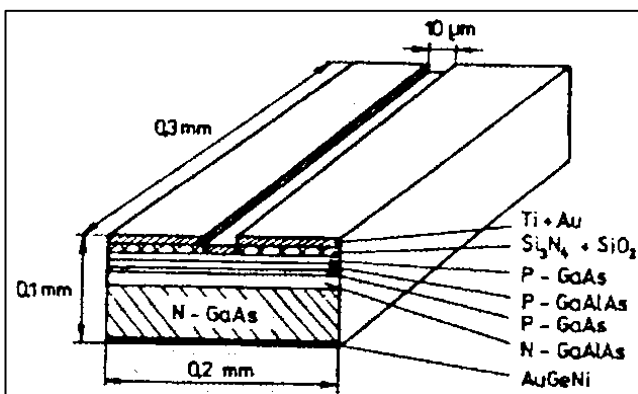
Device MBE suitable for growth of  $A^{III}B^V$  semiconductors layers consists of two to three UHV chambers made from stainless steels (Fig. 5.25). All chambers have UHV pumping systems (usually ionic – sorptive, cryogenic or titanium sublime vacuum pumps). Growth chamber includes in addition the large-scale frozen cryo-panels with liquid nitrogen. Each from together connected chamber has a special purpose, e.g. insertion and preparation of samples, analysis and growth. UHV is important therefore to prevent the contamination surface of growing epitaxial layers and resulting fixation impurities in the volume of layers. The total limit of pressure reaching in systems MBE is of the order  $10^{-8}$  to  $10^{-9}$  Pa. To achievement of the homogenous growth rate (or constitution in multi-component layers) on big substrates it is necessary to use rotation.

**Examples of applications:**

Radiation incurred on PN junction in laser diodes spreads to all directions. Carrier injection incurred with the current passage in permeable direction and their recombination is very effective method for conversion of electricity on luminous energy. To development of the luminescent diodes and namely laser diodes it is of cardinal importance the discovery of super-injection in the double hetero-structure. The active recombination region is in this case surrounded by layers (GaAl)As P- and N-type with bigger width of the forbidden band and with the smaller refractive index – see Fig. 5.26. Such ordering has very favourable influence on own recombination processes and on optical, resp. light guide characteristics of the whole luminescent system.



**Fig. 5.25** Scheme of the MBE growth chamber (sample is placed in the centre of chamber on the rotating holder)



**Fig. 5.26** Hetero-structural semiconductor laser

Today commercially produced **Quantum Well (QW) lasers** reach a big optical power (several W) in the continual regime and make possible to tie up into the fibres, their achievement is bigger than 200 mW. Fundamental technology is the growth of epitaxial structures from metal-organic VPE (method MOCVD) or using MBE method, eventually the combination of both. For effective radiation generation is today most often

exploited the double hetero-structure formed by PN junction – Fig. 5.26.

**Application:** Optoelectronic devices on the base of  $A^{III}B^V$  compounds, transistors freshening the oscillation frequency on several tens GHz, semiconductor lasers, amplifiers of super-fast detectors, photo-detectors and excitors of laser diodes, stabilizers of light impulses, delimiters, multiplexors and demultiplexors, bipolar circuits and so on. It makes the possible their usage in many branches at processing information (e.g. telecommunication).

## 5.5 DIFFUSION

### Diffusion, fundamental terms and mechanism of the diffusion

All reactions between two substances are subjected to the mutual transposition of elementary particles. This transposition is known as **diffusion**. Diffusion is phenomenon, when happens a transfer of particles (atoms or ions). Atoms diffusion of pure metal, which is concerned with the same kind of atoms, is called **self-diffusion (auto-diffusion)**. Diffusion in alloys, which is concerned with migration of different kinds of atoms, is known as **hetero-diffusion**. Principle of this transposition is at self-diffusion the straightening of kinetic energy at the thermal motion of individual atoms (Brownian movement). At hetero-diffusion is process led mostly with the tendency to equalization the chemical concentration differences by atoms transfer in direction of concentration gradient, i.e. from sites with higher concentration to the sites with lower concentration. Common feature and driving force of diffusion is the tendency of the system to achieve higher thermodynamic stability, which can be achieved at different cases either thanks to equalization of the chemical potential or phase transformation under increasing of the chemical concentration differences.

Flow of migrant particles  $J$  of element A in time  $t$  in the direction  $x$  through unit plane perpendicular to this direction at concentration gradient  $\partial c / \partial x$  represents **I. Fick law:**

$$J = -D \left( \frac{\partial c}{\partial x} \right), \quad (5.8)$$

where constant of proportionality  $D$  is **diffusion coefficient** and it is determined generally in  $\text{cm}^2 \cdot \text{s}^{-1}$ . Validity of the above relation is restricted with presumption that the  $D$  is not dependent on the concentration, on the position and distance, does not discount to the defects in material, potential gradient, temperature, tension etc.

From conditions for preservation of the total quantity atoms and molecules diffused substance A it is possible to express also time concentration change in chosen place at the plane by means of the **II. Fick law:**

$$\frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial x^2} \right). \quad (5.9)$$

Solution of this differential equation depends on the initial and edge conditions. Here we bring only final terms for two cases:

a) Diffusion under the conditions of the constant surface concentration  $C_o$  (unlimited diffusion source)

$$C(x, t) = C_o \operatorname{erfc} \left( \frac{x}{2\sqrt{Dt}} \right), \quad (5.10)$$

where supplement of the error function  $\operatorname{erfc}(z) = 1 - \operatorname{erf}(z) = 1 - \frac{2}{\sqrt{\pi}} \int_0^z \exp^{-y^2} dy$  (5.11)

b) Diffusion from the limited source, i.e. from infinitely thin layers into unconfined body

$$C(x, t) = \frac{C_p}{2\sqrt{Dt}} \exp \left( -\frac{x^2}{4Dt} \right), \quad (5.12)$$

where  $C_p$  is the the total quantity of diffused material, i.e. total number of atoms outspread on the unit surface [in  $\text{cm}^{-2}$ ], or surface concentration of the diffused substance.

Coating of admixtures on the substrate surface can be realized by using of several technologies:

- thin layers deposition of impurity or compounds containing an admixture,
- coating of admixture in the form of saline solution on the substrate surface,
- leaching of admixture or its compounds on the surface by the sorption from solution,
- ionic implantation,
- short - term diffusion under the conditions of the constant surface concentration.

**Diffusion coefficient**  $D$  is dependent on the temperature according to the **Arrhenius formula** – see (5.13). The value of activation energy  $Q$  is bigger (or it is necessary to give more energy for the atoms jump), the diffusion is slower.

$$D = D_o \exp \left( -\frac{Q}{RT} \right), \quad (5.13)$$

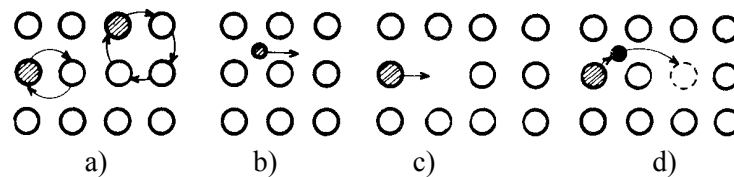


$D_0$  - constant dependent on the character of material, but independent on the temperature and concentration, it is called also frequency factor [ $\text{cm}^2 \cdot \text{s}^{-1}$ ],  
 $R$  – the universal gas constant [ $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ],  
 $T$  - thermodynamic temperature [K],  
 $Q$  - activation energy of diffusion [ $\text{J} \cdot \text{mol}^{-1}$ ].

### Diffusion mechanisms

In crystalline materials are regular atoms in nodal points of the crystal lattice, where occupy the power advantageous position. Point defects are found here too. Owing to oscillations of the lattice (thermal motion of atoms) can come to a jump of atoms from the one equilibrium position to the other, which constitutes diffusion process. According to way of jumps we can distinguish the next diffusion mechanisms – see Fig. 5.27:

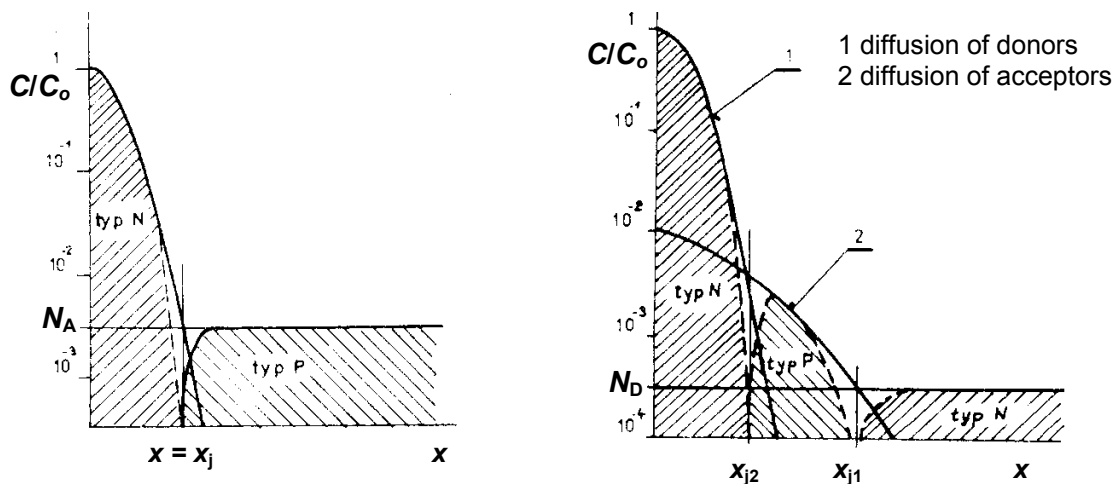
- substitution mechanism (double or cyclic exchange of atoms in nodal point of the lattice) – Fig. 5.27 a),
- interstitial mechanism (migration of atoms from the one among-nodal position to the second – Fig. 5.27 b),
- vacant mechanism (migration of an atom on the vacancy place) – Fig. 5.27 c),
- interstitial substitution (or dissociative) mechanism (atoms walk up from substitution positions to the interstitial, migrate on the interstitial positions and in the place of vacancy they walk again to the substitute position) – Fig. 5.27 d), e.g. diffusion **Cu in silicon**,
- migration of atoms along the linear and plane defects.



**Fig. 5.27** Basic conception of diffusion mechanisms

### Application of diffusion in semiconductor engineering

In production of integrated circuits we need to inject on chosen sites of Si substrate the electrically active admixtures like boron, phosphorus, arsenic or antimony to certain and exactly defined depths at given concentration profile of dopants. To this it is necessary relatively high temperature. Diffusion temperatures are usually in the interval from 900 to 1200 °C. The rate of admixture diffusion into Si depends on type of the additives, temperature of the Si substrate, time and concentration of the dopants and on used atmosphere. Admixtures are on Si substrate distributed in two forms: as elements (B, P, A, Sb) or as oxides ( $\text{B}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ ). Examples of concentration profiles of donors and acceptors in Si are mentioned on Fig. 5.25.



**Fig. 5.28** Concentration of donors and acceptors after gradual diffusion of phosphorus and boron in Si. On the left: NP junction (example of the semiconductor diode), on the right: NPN junction (transistor)

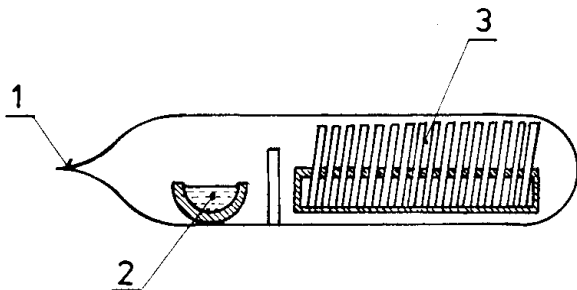
## Diffusion technologies

As the source of the admixture in Si and Ge can be used vapors or liquid films of the elements 3. or 5. groups periodic table, eventually their allied substances. Thin films as diffused source are created using the chemical reaction of vapors with semiconductor surface. The liquid film can be formed also with alloy, which will originate, if the vapor pressure of an admixture at diffusion temperature is bigger than is the solubility in solid semiconductor. Diffusion of admixture atoms proceeds at temperatures  $100 \div 200$  °C below the melting point of semiconductor.

Except the source with endless capacity is used also the source with constant amount of admixture. It is realized using deposition of the element on the semiconductor surface. It is difficult, therefore it is usually created from the planar source with pre-diffusion, namely in short time at lower temperature or alternative method is the deposition of the element using chemical reaction to create the glass layer on the semiconductor surface. As an example may have been a diffusion of phosphorus from  $P_2O_5$  vapors.  $P_2O_5$  acts on a substrate as far as creates the phosphorus-silicate glass. Phosphorus from here diffuses into semiconductors and creates N-type semiconductor layer. The glass layer is then etched.

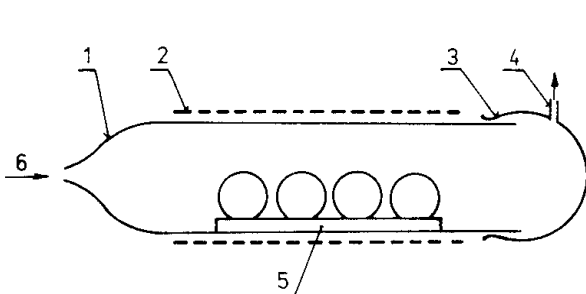
## Diffusion equipments

- 1. Diffusion in the vacuum system with one temperature zone** proceeds in the closed evacuated quartz tube, in which is found semiconductor and admixture. The tube is placed in the oven warmed at required temperature. Vapor pressure is given by amount of the admixture and its temperature.
- 2. Diffusion in the system with one temperature zone under atmospheric pressure** is carried out on air or in flow of the suitable gas (e.g. in nitrogen) – see Fig. 5.30. Admixture is deposited on the semiconductor surface in the form of boron-silicate or phosphorus-silicate glass.
- 3. Diffusion in vacuum with two temperature zones** - see Fig. 5.29. In the first zone (on the left) with the source of admixture is maintained temperature corresponding to the vapor pressure of admixture. In the second zone proceeds the diffusion. In vacuum is evaporation rate of silicon comparable with the diffusion rate.
- 4. Diffusion in the system with two temperature zones under atmospheric pressure.** Vapors are transferred with carrier gas (e.g. nitrogen). Distribution of admixtures depends on the temperature. Diffusion of admixtures into semiconductors proceeds several hours at high temperatures.



**Fig. 5.29** Diffusion in the closed tube with two temperature zones

- 1 – quartz sealed ampoule,
- 2 – source of the diffused substance,
- 3 – semiconductor wafers.



**Fig. 5.30** Diffusion in the open tube with one temperature zone (atmospheric pressure, flow system)

- 1 – quartz tube,
- 2 – tube furnace,
- 3 – quartz finger notch,
- 4 – delivery of waste products,
- 5 – bearer with semiconductor wafers,
- 6 – gas inlet

### Sources of admixtures:

- pure elements (P, As, Sb, Ga ...),
- oxides ( $P_2O_5$ ,  $As_2O_3$ ),
- halides ( $BCl_3$ ,  $BI_3$ ,  $BBr_3$ ),
- silicate layers on the semiconductor surface ( $B_2O_3 \cdot SiO_2$ ). They have low melting point and create the continuous layer on the semiconductor surface.

**Table 5.1** Values of diffusion parameters for self-diffusion and hetero-diffusion of elements in silicon

| Metal       | $Q$ [kJ·mol <sup>-1</sup> ] | $D_0$ [cm <sup>2</sup> ·s <sup>-1</sup> ] | Element in Si | $Q$ [kJ·mol <sup>-1</sup> ] | $D_0$ [cm <sup>2</sup> ·s <sup>-1</sup> ] |
|-------------|-----------------------------|---|---------------|-----------------------------|---|
| Cu          | 197.1                       | 0.2                                       | Cu            | 96.3                        | 0.04                                      |
| Ag          | 184.6                       | 0.4                                       | B             | 355.04                      | 17.1                                      |
| Ni          | 279.6                       | 1.3                                       | Al            | 334.87                      | 8.0                                       |
| Pb          | 101.3                       | 0.28                                      | P             | 365.88                      | 10.5                                      |
| Fe $\alpha$ | 239.4                       | 1.9                                       | As            | 344.32                      | 6.52                                      |
| Nb          | 439.5                       | 12  | Sb            | 381.01                      | 5.6                                       |
| Ta          | 413.1                       | 0.12                                      | Au            | 108.02                      | 0.0011                                    |

## 5.6 METAL DEPOSITION, SPUTTERING AND ION IMPLANTATION

### 5.6.1 Vapor plating and sputtering

At the **vapor plating (metal deposition)** we heat up the material intended for vaporization above its boiling temperature in **high vacuum** and rising vapors are deposited on the substrate. At cathodic **sputtering** happens the rising of the **glow discharge** in atmosphere diluted inert gas and with the positive particles in the plasma is bombarded the cathode containing material intended to sputtering. Material of the cathode begins to sputter and depose on placed substrate.

At the **vapor plating** must be material intended to vaporization set on the heat source, e.g. inside resistance heating spiral. Evaporated material can be placed also nearby of the tungsten cathode. This technology was exploited for vapor plating of barium as getter at production of electronic tubes and vacuum TV screens.

**High-frequency sputtering** makes it possible for pulverization of non-metallic materials too. One from the advanced methods of the formation of thin layers and coatings is **magnetron sputtering**, based on the principle of the sputtering of stationary target. It concerns about a physical process, when pulverized atoms are deposited on the surface articles (substrates), which are electroplated and form the coating with required constitution. This technology makes it possible to deposit pure metals, alloys and compounds. Layers of pure metals and alloys like e.g. Cu, Al, Cr, Ag, Cr- Ni, brass, bronze, stainless steel are deposited in pure argon. Layers of compounds are formed at reactive sputtering, e.g. ZrN sputtering of Zr in the Ar + N mixture. Coating can be sputtered on substrates made from metals, plastic material, glass, ceramics, but also on very thin foil.

Magnetron sputtering is successfully used in microelectronics, optics, machine engineering, automotive and aircraft industry, packaging technology, glass industry, bijouterie and in next spheres for deposition of functional and decorative coatings.

**Targets** (cathodes) for sputtering are usually of circular or rectangular shape. The active layer is connected with the substrate, it must have big heat conductivity, the apparatus must be vacuum tight. This enables the effective cooling of target by flowing water.

For sputtering of the conductive paths in microelectronic components (chips) are used targets with active layer from aluminum - silicon - copper alloy. Silicon prevents the dissolving of aluminum into silicon substrate in places contacting micro-wires. Copper restricts the migration of the deposited aluminum.

### 5.6.2 Metallization of silicon with the Al-Cu-Si alloy

A lot of transistors, diodes, capacitors and resistors are placed in every chip of the integrated circuit (IO). As soon as are these elements of IO on Si board made, it is necessary them electrically connect by means of conductive thin-film. Further it is necessary to create the conductive contact facets or expanded contacts on the microchip, that interconnect by means of very thin (average 25  $\mu\text{m}$ ) gold or copper wires the metal set supplies inside of IO. Basic material for the conductive connection of elements in the microchip is aluminum doped with copper and silicon.

Principle of the **sputtering** method consists at first in the preparation of the target from Al-Cu0.5-Si1 alloy made from highly pure materials (99.999 %) – see Fig. 5.31. Target is bombarded in vacuum with argon (Ar<sup>+</sup>) ions purity 99.999 %, which come out Al, Cu and Si atoms from target in the ratio near, in which were found in the target. These atoms are then deposited on Si boards at rising of Al-Cu-Si layers with thickness about 2  $\mu\text{m}$ .

Sputtering proceeds at the pressure  $1 \cdot 10^{-1}$  Pa at the temperature of Si wafers around 200 °C. Infrared (IR) heater of Si wafers is placed in the deposition equipment for sputtering. Before the deposition are wafers warmed on cca 200 °C, to increasing of Al, Cu and Si atoms mobility in Si. Electric voltage on the target (cathode) is about 900 V. The energy of  $Ar^+$  ions, that are created thanks to the electrical discharge between cathode and anode, is then about 900 eV. About 75 % of  $Ar^+$  ions energy after their fall on the Al-Cu-Si target is changed in warm. That is why the Al-Cu-Si target must be outwardly intensively cooled with water. Al-Cu-Si layers with thickness 2  $\mu m$  are deposited on Si wafers during 50 minutes. 60 pieces of Si wafers with diameter 100 mm are placed on the rotary drum in one charge. 4 targets are installed in the deposition equipment. Total utility of the target is about 30 %.

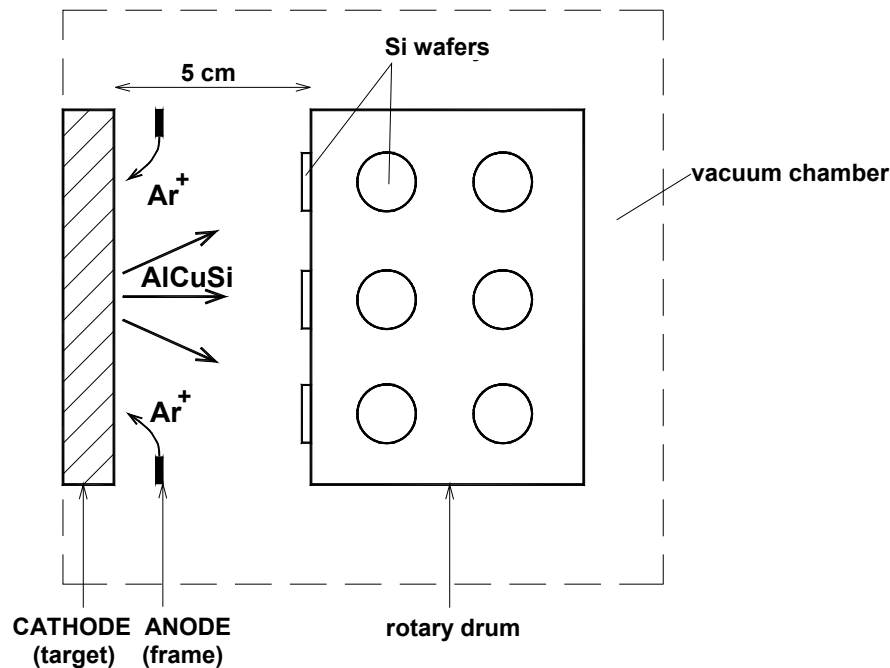


Fig. 5.31 Principle of the sputtering method (metallizing of Si wafers with Al-Cu-Si alloy)

One of the important quantities determining the sputtering rate of individual components in Al-Cu-Si alloys is so-called **sputter yield**. It is relationship of the number of atoms sputtered component released from target through one  $Ar^+$  ion. Sputter yield is dependent on a kind of sputter material, and on energy of inert gas.

### 5.6.3 Ion implantation

It is a process at which are electrically charged atoms of admixtures ( $B^+$ ,  $P^+$ ,  $As^+$ ,  $Sb^+$ ) implanted into the Si substrate. Energies of the positive ions of admixture are very high, typically in range 40 ÷ 180 keV. Electric voltage used at ion implantation is about 100 kV, i.e. energy of one electron is 100 keV in this case. At these energy has an electron rate 187000 km/s. At the drop of potential 100 kV, would be speed of  $As^+$  ions about 500 km/s, because the rate of charged particles in electric field is indirectly proportional to the square root of their weight.

**Ion implantation** is very accurate and reproducible process for landing of admixtures in the form of elements on Si wafers. The penetration depth of implanted ions hardly depends on their energy and kind of the ions. The same is true for penetration of implanted ions into masking  $SiO_2$  layers. The largest penetrations has boron  $B^+$ , because of their smallest ionic radius. The smaller is ion, the better is penetration between the Si atoms spaces in its lattice or between Si and O atoms in amorphous  $SiO_2$ . At ion implantation happens the shooting of elements into very shallow area of Si. This Si region with the thickness round 0.1  $\mu m$  is then saturated with admixture element and can be engaged as a source for diffusion.

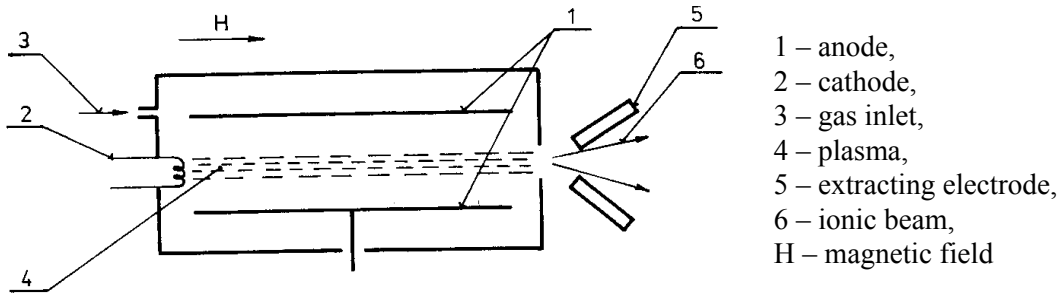
$B^+$ ,  $P^+$ ,  $As^+$  and  $Sb^+$  ions are extracted in the implementing equipment by the ionisation of compounds with the appropriate elements. Mostly are used compounds with fluorine or chlorine ( $BF_3$ ,  $PCl_3$ ,  $AsF_3$ ,  $SbF_5$ ). These substances are considerably volatile, very toxic and corrosive.

Ions are accelerated on the required energy and cations ( $B^+$ ) from anions ( $F^-$ ) are separated. Cations ( $B^+$ ) are then implemented into Si wafer. Process of the ions accelerating, their separation and implementation (shooting) of cations into Si wafers proceeds in high vacuum  $10^{-4}$  Pa. This vacuum is obtained by means of the cryogenic vacuum pumps.

Among the most widely known ionic sources belong the sources with cold cathode and with hot cathode.:

**Ion source with cold cathode** uses the known Penning's principle. At application of high electric voltage on the electrodes (several kV) are emitted electrons from the cold cathode. Their path from cathode to anode, during the colliding of electrons with gas molecules happens to the ionization. It is prolonged thanks to enclosed magnetic field. Penning's sources are used exclusively to gas ionization from gaseous media and produce the ionic beam with the flow until several hundreds mA.

**Hot cathode ion source** uses next principle: Between the anode and heating cathode burns appearance to high gas pressure ( $1$  to  $10^{-2}$  Pa) stationary electric arc. Electrons path is prolonged thanks to magnetic field. In the ion source (see Fig. 5.32) happens the ions extraction in direction longitudinal to the axis of plasma. From the ion source is extracted ionic beam with circular section, diameter about  $0.5$  mm. It is appropriate for the implantation from gaseous media, but also from solid-state materials, because it is invested with an electric oven with temperatures about  $1800$  °C.



**Fig. 5.32** Principle of the hot cathode ion source

# 6. SEMICONDUCTIVE MATERIALS

## INTRODUCTION

**Semiconductors** are materials which, at low temperature, behave like insulators, and like conductors at higher temperatures; their resistivity at normal temperature  $\approx 298$  K is  $\rho$  conductors  $< \rho$  semiconductors  $< \rho$  insulators. Semiconductor conductivity rises (unlike conductors) and has electron – hollow character (unlike insulators).

**Resistivity thermal dependence of metals:**

**Resistivity thermal dependence of semiconductors:**

$$\rho_m = 1 / \sigma = \rho_o (1 + \alpha_R \Delta T)$$

$$\rho_p = A \cdot \exp (\Delta W / k T),$$

(6.1)

$\rho_k$  – conductor resistivity (metal) [ $\Omega \cdot m$ ],

$\rho_o$  – resistivity at  $T_o = 293$  K [ $\mu\Omega \cdot cm$ ],

$\sigma$  – conductivity (el. conductivity) [ $S \cdot m^{-1}$ ],

$\alpha_R$  – temperature coefficient of el. resist. [ $K^{-1}$ ],

$\Delta T = T - T_o$  – temperature difference [K],

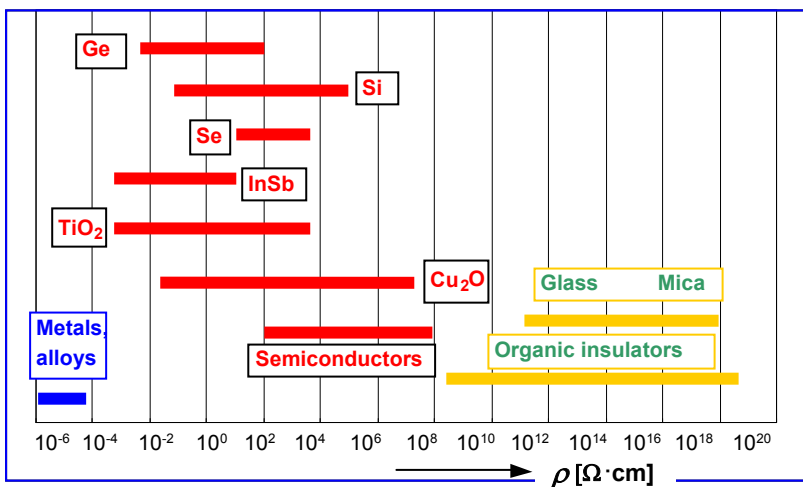
$\rho_p$  – semiconductor resistivity [ $\Omega \cdot cm$ ],

$k$  – Boltzmann constant  $8.617 \cdot 10^{-5}$  eV  $\cdot K^{-1}$ ,

$A$  – frequency factor (pre-exponential factor) [ $\Omega \cdot cm$ ],

$\Delta W$  – forbidden band width [eV],

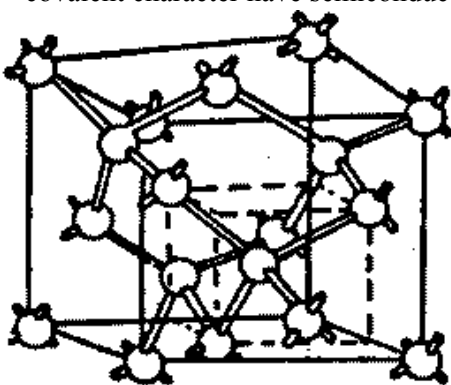
$T$  – temperature [K].



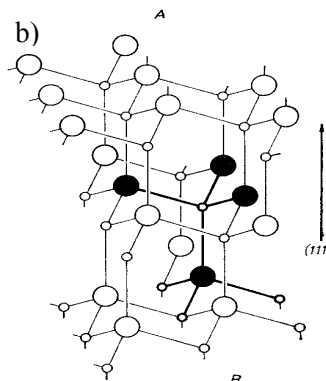
**Fig. 6.1** Resistivity ranges of materials for electrical engineering

## 6.1 SEMICONDUCTOR MATERIAL STRUCTURE AND ATOMIC BOND

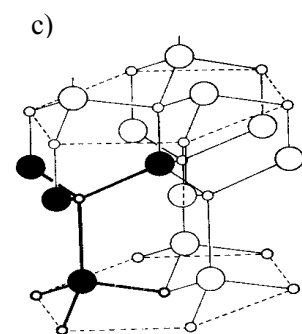
Silicon and germanium have the diamond type lattice structure – Fig. 6.2 a) semiconductor compounds have the sflerite (ZnS) or wurzite (FeO) type lattice – Fig. 6.2 b), c). Elementary cell of **diamond lattice** comprises of eight atoms: one atom in each of the 8 corners, six atoms on 6 faces and 4 atoms are inside the cube with lattice parameter  $a$ . In this configuration, each atom inside the crystal is bonded only with 4 of its closest neighboring atoms placed in space in the same distance. **Coordination number** of most of the semiconductive materials is  $Z = 4$ . Bond between atoms in element semiconductors (Si, Ge) is **covalent, ion-covalent** bond with predominantly covalent character have semiconductive compounds (GaAs, CdTe...).



a) diamond lattice



b) cubic (sflerite ZnS type)



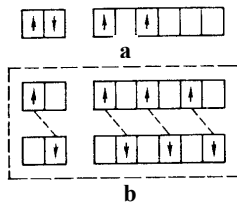
c) hexagonal (wurzite FeO type)

**Fig. 6.2** Schema of atom spatial configuration in Si and in A-B semiconductive compounds

### 6.1.1 Bond hybridization

Both silicon and germanium crystallize in diamond lattice (Fig. 6.2a) and are characterized by typical covalent bond. **Covalent bond** comprises of electron pairs with opposite spin moments on the same energy level. Four atoms (neighboring) are symmetrically arranged around each atom in semiconductive material; they are all connected to the central atom by bond facilitated by single valence electrons. Central atom is in the middle of tetrahedron, its corners represent the four closest atoms. Two neighboring atoms of crystal share two electrons, exchanging them; it cannot be differentiated which electron belongs to which atom. Any atom of the lattice is therefore surrounded by eight electrons; half of each of those electrons belongs to this atom. Electron octet is important mostly for maintaining the electro-neutrality of the atom, since atom therefore achieves the electron configuration of inert gasses He, Ne, Ar, ...

**Bond hybridization principle:** Isolated Si atom has the valence shell configuration of  $(ns)^2(np)^2 - s^2p^2$  for short, where  $n$  is the main quantum number – Fig. 6.3 a). To achieve the electron octet the atom must share another four electrons from four closest atoms with the same valence shell configuration. This however violates Pauli principle,



since there can be only two electrons in  $s$  orbital (with opposite spin). Each Si atom must therefore place one electron to the higher-energy orbital  $p$ , and each of those atom therefore has the  $(ns)^1(np)^3$  shell configuration,  $sp^3$  for short - Fig. 6.3 b). Hybrid tetrahedron bonds  $sp^3$  are typical for all elementary and compound semiconductors; all atoms with covalent bond hybridize this way. The angle between the axes defined by the atom couples is  $109^\circ 28'$ . The contraindication of the hybridization is high inner energy between atoms which, from physico-chemical point of view, exhibits itself by high melting point, high hardness and high molar enthalpy of melting compared to the metallic materials – comparison with common metals is in Table 6.1.

Fig. 6.3 Principle of bond hybridization in Si

Table 6.1 Melting points, molar melting enthalpy and entropy of chosen metals and semiconductors

| Metal | $T_m$<br>[°C] | $\Delta H_m$<br>[J·mol <sup>-1</sup> ] | $S_m$<br>[J·mol <sup>-1</sup> ·K <sup>-1</sup> ] | Semiconductor | $T_m$<br>[°C] | $\Delta H_m$<br>[J·gat <sup>-1</sup> ] | $S_m$<br>[J·gat <sup>-1</sup> ·K <sup>-1</sup> ] |
|-------|---------------|--|--|---------------|---------------|--|--|
| Cu    | 1083          | 13437                                  | 9.91   | Si            | 1420          | 46470                                  | 27.45  |
| Ag    | 961           | 11300                                  | 9.16   | Ge            | 940           | 34720                                  | 28.62  |
| Al    | 660           | 10800                                  | 11.58  | GaAs          | 1238          | 52600                                  | 34.83  |
| Fe    | 1538          | 15200                                  | 8.4  | GaP           | 1511          | 62700                                  | 35.16  |
| Ni    | 1453          | 17920                                  | 10.38  | GaSb          | 706           | 32400                                  | 33.08  |

### 6.1.2 Generation and recombination of charged particle

Perfectly pure semiconductor contains, at low temperatures, no free electrons to facilitate current flow. Electrons of outer orbitals are held in their places by covalent bonds. Semiconductor at low temperatures thereby behaves like an **insulator**. **Valence band of a semiconductor, at temperature  $T = 0$ , is completely filled with electrons, conduction band is empty. There is band gap of  $\Delta W$  width between the two ones.** Some energetic states can occur in the band gap due to the imperfections of crystal lattice.

Increase of the temperature results in some valence electrons breaking away from their bonds due to the thermal motion. Even at normal temperatures, small amount of electrons can move through the lattice outside of their bond. Resulting empty spot in valence bond is called a **hole**. It is, in fact, a place with a lack of negative charge. The hole therefore acts as positive charge. This phenomenon is called **generation of charged particles**. Holes, same as **free electrons**, can freely move through the lattice. The transport is facilitated by other electron from neighboring bond jumping to the hole. Thus the hole basically switches places with electrons and shifts. Repetition of this process facilitates the motion of the holes.

Concentration of electrons and holes in the thermal equilibrium corresponds to the equilibrium concentration of electrons and holes. During the motion of free electrons through crystal lattice, free electron can collide with a hole, resp. empty place in valence bond. This collision fills the bond. This phenomenon is called **RECOMBINATION**. During recombination, one free electron and one hole disappear and certain quantum of energy is released (thermal, photon, phonon). At normal temperature, small amount of electrons is being continually released, and also continually recombines with holes. Superfluous charged particles are unstable  $\Rightarrow$  they recombine.

**Direct RECOMBINATION** (inter-band) – electron from conductive band can jump to the vacant place in valence band. Excessive energy is transmitted to the crystal lattice in form of phonon.

**RECOMBINATION** facilitated by **recombination center** (typically other atoms) in natural or artificial lattice defects. Their energy states lie inside the band gap. Electron passes from conductive band to the recombination center, where it reacts with the hole from valence band.

**Recombination consequences:**

- Dissipation of energy in vicinity – radiation (photon).
- Collision with crystal lattice or with free charged particles (phonon).

## 6.2 SEMICONDUCTOR CONDUCTIVITY

### 6.2.1 Intrinsic conductivity of semiconductor

Regarding the band theory, the material can become conductive if one of its bands isn't fully occupied, since there are energetic states available for electrons with sufficient energy to make the jump from lower to higher energetic state. According to the **Pauli exclusion principle**, there can be no conductivity in fully occupied band, because there are no energetic states available for electrons to jump to.

Temperature is also important for conductivity. Heating of a crystal causes atoms to vibrate around their stable position. Energy quantum, corresponding to these vibrations, is called phonon. **Phonon** is a clump of oscillations or waves, able to freely move through the lattice. At temperatures above 0 K, the material fills up with phonons. Phonons and electrons move rapidly. They collide and exchange energy.

The valence electron must pass the band gap (jump from the valence band to the conductive band) to become free and therefore able to constitute current flow. At room temperature, there is about  $10^{10}$  of free electrons (due to the charged particle generation) in  $1 \text{ cm}^3$  of silicon and germanium contains about  $10^{13}$  electrons in  $1 \text{ cm}^3$ .

**Intrinsic conductivity** of semiconductor is thus facilitated by charged particle generation of the basic (pure) semiconductive material. Electron and hole is always formed at the same time, i.e. two charged particles form in the crystal lattice regardless of the type of non-intrinsic conductivity.

### 6.2.2 Non-intrinsic (doped) conductivity of semiconductor

**Non-intrinsic conductivity** of semiconductor is facilitated by artificially added impurities – micro-alloying. Effect of impurities on conductivity is immense. Small concentrations of impurities increase the conductivity by ten orders of magnitude (based on impurity concentration). One atom of impurity per  $10^{10}$  atoms of the basic material already produces significant increase of the conductivity. In electrical engineering, atoms of other elements than the basic material are often added. These added atoms most frequently replace the atoms of the original semiconductor lattice atoms. Materials with impurities exhibit both intrinsic and non-intrinsic conductivity. The conductivity of semiconductors can be substantially increased by small amounts of additive. Atoms of the additive replace some atoms of the semiconductor crystal lattice.

Added atoms with more valence electrons than is necessary to form valence bond with four neighboring atoms of silicon or germanium supply the lattice with additional free electrons which can move freely through the lattice. Conductivity of the semiconductor is therefore increased. Additives providing the semiconductor with additional **free electrons** are called **donors**.

#### N - type semiconductor

Semiconductor of the fourth group of periodic table, e.g. silicon and germanium, are usually doped with **fifth group elements** such as phosphorus, arsenic or antimony. Atoms of these elements have one additional electron compared to the Ge and Si. Conductivity in this case is **N-type – electron conductivity**. Each atom of the semiconductor has four valence electrons, dopant atom has five. Four peripheral electrons of dopant form covalent bond with four neighboring atoms of germanium or silicon. The fifth electron is bonded freely by attractive force between the electron negative charge and the positive charge of the dopant atomic core. Electron provided by the donor behaves like free electron. Donor atom which loses its electron becomes cation, firmly fixed in the lattice.

#### P - type semiconductor

Germanium and silicon can be also doped with atom with less electrons than is necessary to form valence bonds with surrounding atoms of semiconductor. In this case, some of the bonds are not completely filled, and a **holes** occur. Dopants of this type are called **acceptors**. Conductivity is therefore **P-type – hole conductivity**. Formed hole can be filled with electron and the result is the same as if a positive charge moves thus providing electric current. Acceptor atoms add another energy state above the band gap in the band diagram, right under the valence band. The distance between the gaps is so low, that most of the acceptor atoms are ionized at room temperature, thus forming holes.



Semiconductors of the fourth group of periodic table Ge and Si are doped with acceptors from **from the third element group**. Those are for example boron, aluminum, gallium and indium. The outer shell of these atoms has one less electron than the shell of germanium or silicon. Each semiconductor atom has four valence electrons, the dopant atom has only three. One valence bond is therefore not completely occupied, and a hole is formed.

Actually, there are always some holes in an N-type semiconductor and some free electrons in a P-type semiconductor. It is thus more correct to define the N-type semiconductors as a conductor where the number of free electrons greatly outweighs the number of holes and P-type semiconductors as a conductor where the number of holes outweighs the number of free electrons. Charged particles predominating in the semiconductor and thus define the type of its conductivity are called **major charge carriers**. The opposite charged particles are called **minor charge carriers**. The minor carriers in material with non-intrinsic N-type conductivity are holes, in non-intrinsic P-type conductivity electrons. Electron in such semiconductor placed in electric field move from positive electrode to the negative one. From the outside, this manifests as current flow.

**Compensation ratio  $K$**  is described by

$$K = N_{\min} / N_{\text{maj}} \quad (6.2)$$

$N_{\text{maj}}$ ,  $N_{\min}$  – concentration of major, resp. minor carrier [ $\text{cm}^{-3}$ ].

**Lifetime of the minor charge carriers** characterizes „inertia“ of the recombination processes and is an important attribute for correct function of semiconductive components – transistors and diodes.

The conductivity of both P-type and N-type is generally called **extrinsic** or **dopant conductivity**, unlike the conductivity of pure semiconductors. Ionization of pure germanium or silicon produces mobile electron and mobile hole, while ionization of additive produces one mobile charge carrier and one immobile ion.

Trivalent and pentavalent element compounds also exhibit semiconductive properties. The ratio between the two atom types must be 1:1, so there are eight valence electrons. Atoms of these elements are bound by **covalent bond** (i.e. **reciprocal sharing of valence electron couples**), both atoms have valence shell filled with four electrons.

In principle, any combination of trivalent (B, Al, Ga, In) and pentavalent elements (N, P, As, Sb) can be used. To achieve non-intrinsic P-type conductivity, bivalent (Zn), or hexavalent (Te) dopants are used. These materials – intermetallic semiconductors, have an excellent electron mobility compared to silicon and germanium (GaAs has about five times higher electron mobility compared to silicon). This property is utilized especially in production of high-frequency components.

Based on the effect on semiconductive material conductivity, the elements can be divided in several groups:

➤ **ELECTRO-NEUTRAL ELEMENTS**

- A) **Interstitial (interstitial) elements** are placed in inter-nodal points of the lattice and provide no free charge carriers. They therefore do not directly bond with the atoms of semiconductor in nodal positions.
  - B) **Isovalent (isomorph) elements** are in the same group as the basic element e.g. Ge in Si or Al in GaAs. They have same amount of electrons as the element that substitute. They therefore do not alter the conductivity, however they affect other physical properties of the semiconductor, e.g. change lattice parameters, band gap widths, change of wavelength of semiconductor lasers and so forth.
  - C) **Inert elements** which do not form any kind of bond with the semiconductor (e.g. inert gasses He, Ne, Ar...).
- **DONOR ADDITIVES** – provide one additional electron than is necessary to form valence bond. These elements are in the column right next to the substituted element (e.g. As in Si, In in CdTe or Te in GaSb).
- **ACCEPTOR ADDITIVES** – lack one atom, needed to form full covalent bond (one hole per atom is created). These elements are in the column on the left of the substituted element column (e.g. Al v Si, Ag v CdTe or Zn v GaSb).
- **ADDITIVES CAUSING LOW LEVELS OF CONDUCTIVITY** – provide two or more additional electrons per atom than is necessary to form full covalent bond or two or more holes. This significantly deteriorates electric field in the semiconductor. These elements are at least two columns to either side from the column of the substituted element (e.g. Cu in Si, Fe in CdTe or Ag in GaSb). The elements of this group are basically all transition metals, i.e. all elements with not-fully occupied inner shells - all elements in Ib, IIb to VIIIb columns of periodic table. These elements have severe detrimental effect and they can cause destruction of the whole chip because of the local increase of current density consequently increasing temperature, the working point of the diode or transistor is thusly changed and eventually a failure occurs. This is why must the sum of these elements be lower than  $10^9$  to  $10^{10}$  atoms per  $1 \text{ cm}^3$  of Si. Consequently, this means 1 atom of the impurity per  $10^{12}$  of Si atoms. Some micro-alloying elements such as Ni and Cr in

so called **semi-insulating** GaAs (semiconductor with high resistivity), present an exception for this rule. Addition of these elements eliminates the detrimental effect of other additives by bonding them chemically or electrically.

- **AMPHOTERIC ADDITIVES** – can be either donor or acceptor, depending on which atom in the  $A^{III}B^V$  compound they replace, e.g. if Ge replaces Ga in GaAs, it acts as a donor, since it has one extra electron compared to Ga. Conversely, if Ge replaces As, the germanium atom will act as an acceptor, since it lacks one electron necessary to form covalent bond to compared As. Some elements of this type can, in some cases, behave like donors and as acceptor in others –Table 6.2.

**Table 6.2** Behavior of elements in semiconductive materials:

| Semi-conductor | Electro-neutral elements     | Donors                | Acceptors                | Additives with low level of conductivity  | Amphoteric additives                         |
|----------------|------------------------------|-----------------------|--------------------------|---|--|
| <b>Si</b>      | H, N, C, Ge, Sn, Pb, He, Ne, | P, As, Sb, (Li)       | B, Al, Ga, In            | Cu, Au, Zn, Mn, Fe, S, O                  | -  |
| <b>Ge</b>      | H, N, C, Si, Sn, Pb, Ne, Ar  | dtto                  | dtto                     | Cu, Ag, Au, Zn, Cd, Mn, Ni, Fe, S, Se, Te | -  |
| <b>GaP</b>     | H, N, B, Al, In, As, Sb      | S, Se, Te, Si, Ge, Sn | Be, Mg, Zn, Cd, C, (Cu)  | Cr, Fe, V, O, Ni, Mn, Ag, Au              | Si, Sn (up $10^{18}$ cm <sup>-3</sup> donor) |
| <b>GaAs</b>    | H, N, B, Al, In, P, Sb       | S, Se, Te, Si, Ge, Sn | Zn, Cd, Be, (Li)         | dtto                                      | Si, Ge (up $10^{18}$ cm <sup>-3</sup> donor) |
| <b>InP</b>     | H, N, B, Al, Ga, As, Sb      | S, Se, Te, Ge, Sn     | Zn, Cd, Be, Mg, (Cu)     | dtto                                      | -  |
| <b>InAs</b>    | H, N, B, Al, Ga, P, Sb       | S, Se, Te, Si, Ge, Sn | Zn, Cd, Mg               | dtto                                      | -  |
| <b>InSb</b>    | H, N, B, Al, Ga, P, As       | S, Se, Te, Sn, (Li)   | Zn, Cd, Mg, Si, Ge, (Cu) | dtto                                      | -  |

The relationship between concentration of major carriers and resistivity in semiconductors is approximately:

$$\rho = 1/\sigma = \frac{1}{N_{maj} e \mu_{maj}} \quad (6.3)$$

$\rho$  – semiconductor resistivity [ $\Omega \cdot \text{cm}$ ],

$e$  – electron charge [ $1.602 \cdot 10^{-19}$  C],

$\mu_{maj}$  – mobility of major charge carrier [ $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ ].

$\sigma$  – semiconductor el. conductivity [ $\text{S} \cdot \text{cm}^{-1}$ ],

$N_{maj}$  –major charge carrier concentration [ $\text{cm}^{-3}$ ],

The numerical values of donor and acceptor mobility of selected elementary and compound semiconductor are listed in Table 6.3.

**Table 6.3** Selected physical properties of semiconductive materials

| Semi-conductor | $a$ [cm]              | Density [ $\text{kg} \cdot \text{dm}^{-3}$ ] | $\Delta W$ [eV] | $\mu_D$ [ $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ ] | $\mu_A$ [ $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ ] | $t_M$ [ $^{\circ}\text{C}$ ] | $N$ [ $\text{cm}^{-3}$ ] |
|----------------|-----------------------|--|-----------------|---|---|------------------------------|--------------------------|
| Si             | $5.43 \cdot 10^{-8}$  | 2.33   | 1.12            | 1350  | 480   | 1420                         | $5.0 \cdot 10^{22}$      |
| Ge             | $5.66 \cdot 10^{-8}$  | 5.323  | 0.67            | 3900  | 1900  | 940                          | $4.42 \cdot 10^{22}$     |
| AlSb           | $6.138 \cdot 10^{-8}$ | 4.26   | 1.65            | 900   | 400   | 1060                         | $3.46 \cdot 10^{22}$     |
| GaP            | $5.449 \cdot 10^{-8}$ | 4.13   | 2.26            | 300   | 150   | 1511                         | $4.94 \cdot 10^{22}$     |
| GaAs           | $5.653 \cdot 10^{-8}$ | 5.32   | 1.42            | 8600  | 250   | 1238                         | $4.43 \cdot 10^{22}$     |
| GaSb           | $6.095 \cdot 10^{-8}$ | 5.60   | 0.68            | 5000  | 1000  | 706                          | $3.53 \cdot 10^{22}$     |
| InP            | $5.868 \cdot 10^{-8}$ | 4.78   | 1.27            | 5300  | 100   | 1070                         | $3.96 \cdot 10^{22}$     |
| InAs           | $6.058 \cdot 10^{-8}$ | 5.66   | 0.36            | 33000   | 450   | 940                          | $3.60 \cdot 10^{22}$     |
| InSb           | $6.479 \cdot 10^{-8}$ | 5.77   | 0.17            | 78000   | 7000  | 525                          | $2.94 \cdot 10^{22}$     |

$a$  – lattice parameter,  $\mu_D$ ,  $\mu_A$  – donor, resp. acceptor mobility,  $t_M$  – melting point,  $N$  – amount of atoms in  $1 \text{ cm}^{-3}$

## 6.3 SEMICONDUCTIVE MATERIALS – BASIC CLASSIFICATION

- ❑ **Elementary:** Ge, Si, (Se, Te).
- ❑ **Compound:**  $A^{III}B^V$ ,  $A^{II}B^{VI}$ ,  $A^I B^{VII}$ ,  $A^{IV}B^{VI}$ ,  $A_2^{III}B_3^{VI}$ ,  $A_2^V B_3^{VI}$ , SiC, ...
- ❑ **Ternary and quaternary:** ternary and quaternary solid solutions of  $A^{III}B^V$  or  $A^{II}B^{VI}$  type. These are the basic materials for modern optoelectric structures.
- ❑ **Oxide:**  $Cu_2O$ , ZnO, ferrites, garnets, ferroelectrics.

### 6.3.1 ELEMENTARY SEMICONDUCTORS

#### SILICON

|                                       |   |
|---------------------------------------|---|
| - Electron configuration              | $1s^2 2s^2 2p^6 3s^2 3p^2$  |
| - Proton number                       | $z = 14$  |
| - Relative atomic weight              | $A_r = 28.08$   |
| - Chemical bond between atoms         | covalent  |
| - Crystal structure                   | cubic, diamond type   |
| - Band gap width                      | $\Delta W = 1.12 \text{ eV}$  |
| - Lattice parameter                   | $a = 0.357 \text{ nm}$  |
| - Number of atoms in $1 \text{ cm}^3$ | $N = 5 \cdot 10^{22}$   |
| - Density                             | $\rho = 2.329 \text{ kg} \cdot \text{dm}^{-3}$                      |
| - Melting point                       | $t_M = 1420 \text{ }^\circ\text{C}$                                 |
| - Relative permittivity               | $\epsilon_r = 12.5$   |
| - Mobility of electrons               | $\mu_D = 1350 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ |
| - Mobility of holes                   | $\mu_A = 480 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$  |
| - Donors - V. group                   | (N, P, As, Sb) $\Rightarrow$ N-type semiconductor                   |
| - Acceptors - III. group              | (B, Al, Ga, In) $\Rightarrow$ P-type semiconductor                  |

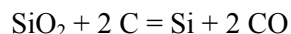
**Si is utilized** exclusively in single crystal form for **semiconductive component** fabrication, e.g. **transistors, diodes, thyristors, integrated circuits, microprocessors, memory modules** etc.

Si has **wider range of operation temperature** and higher reliability and lifetime compared to the Ge components.

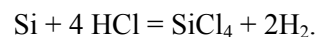
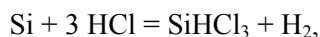
Other Si compounds: SiC,  $Si_3N_4$ ,  $SiO_2$  – insulation and dielectric layers.

Silicon is the second most abundant element in the Earth crust. Silicon cannot occur in the crust in its pure form. Lithosphere comprises of about 25 wt. % of silicon in form of various compounds. The most common silicon compound is **silicon oxide** and various silicates.

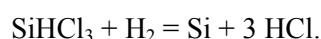
The precursor for **metallurgical silicon** is quartz –  $SiO_2$ ; silicon is produced by reduction of quartz by carbon (coke) in electrical furnaces:



Metallurgical silicon is not suitable for application in semiconductor industry as it contains about 0.2 wt. % of impurities (predominantly aluminum and iron). All methods of high purity silicon production are based on acquiring a suitable compound from metallurgical silicon, its refinement and then decomposition of this compound yielding pure silicon. Silicon halides and halogen silanes are suitable precursors for this process. Nowadays, the **trichlorsilane** –  $SiHCl_3$  is being used almost exclusively; **silicon chloride** –  $SiCl_4$  or **silane** -  $SiH_4$  are also used, but rarely. The first two compounds are produced by reaction between hydrochloride (pure, anhydrous) with milled metallurgical silicon at  $280 \div 380 \text{ }^\circ\text{C}$ . Ongoing reactions are summarized by these reactions:



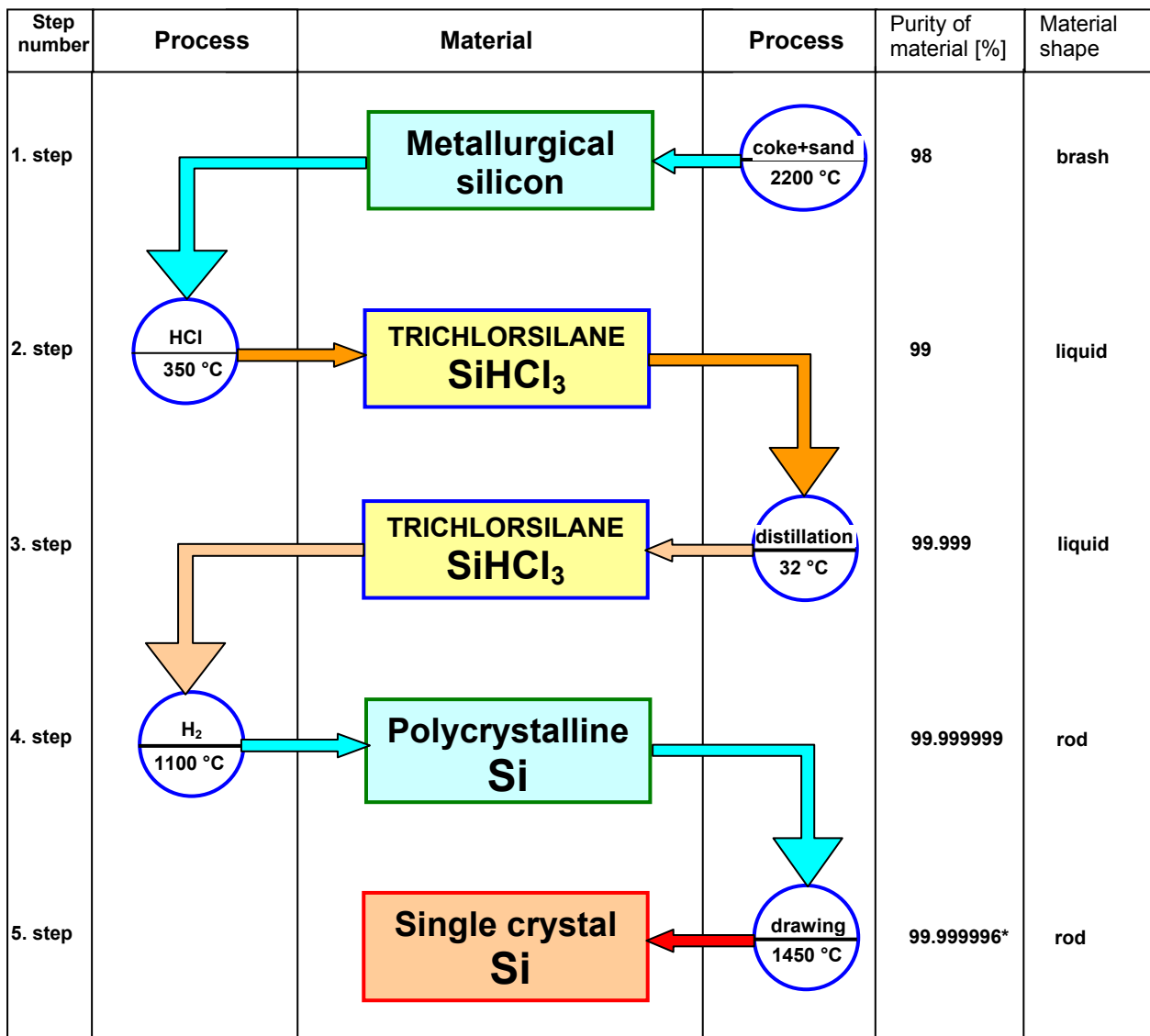
Reaction conditions can be altered to shift the reaction equilibrium to favor one or the other product (either  $SiHCl_3$  or  $SiCl_4$ ). Additives present in the metallurgical silicon react simultaneously to form chlorides ( $FeCl_3$ ,  $AlCl_3$ ,  $BCl_3$ ,  $PCl_3$  and so forth). Formed compounds are then refined ( $SiCl_4$  and  $SiHCl_3$  are liquid at normal temperatures). Refining, i.e. repeated distillation produces high-purity trichlorsilane. Refined trichlorsilane usually contains about 5 ppm of carbon, mostly in form of methyltrichlorsilane  $CH_3SiCl_3$ , phosphorus and boron is kept below 1 ppm. Reverse decomposition of pure trichlorsilane is facilitated by reduction in hydrogen at 1000 to 1100  $^\circ\text{C}$ , summarized by (simplified) reaction:



This decomposition (deposition) of trichlorosilane takes place in steel, water-cooled reactor (deposition device) – silicon rods of several mm thickness, also called **silicon cores**, are placed inside. These silicon rods are electric heated to the reaction temperature. Trichlorosilane vapor with surplus hydrogen is fed to the reactor. Forming silicon deposits on the core (the core is held at the reaction temperature); cylindrical ingot of **polycrystalline silicon** is growing around the core. Structure of this silicon ingot is partially dendritic, partially amorphous. Cylindrical rods of up to 200 mm of polycrystalline silicon are produced industrially utilizing this process. The whole process of rectification of trichlorosilane and his subsequent decomposition is, in practice, carried out continually, i.e. necessary amount of trichlorosilane for production of polycrystalline silicon is taken directly from the rectification column.

Purity of polycrystalline silicon produced this way is high enough to utilize this material in most of the semiconductive microelectronic applications without further purification; the material is worked to produce single crystal of desired dimensions. Limiting factor is the boron content, because boron does not evaporate in vacuum and dissolves in silicon.

Micro-alloying of Si or Ge by boron or phosphorus is usually facilitated by addition of small amounts of diborane ( $B_2H_6$  – gas), resp. fosfine ( $PH_3$  – gas) to reaction mixture right before the decomposition step. Thus produced micro-alloyed rods of polycrystalline silicon are processed to form single crystals with desired additive concentration. Schema of the pure silicon production technology is shown on Fig. 6.4.



**Fig. 6.4** Sequence of technological operations during refining of silicon and production of single crystals

Most of the elements exhibit so called **retrograde solubility** in silicon, i.e. their maximum solubility temperature is bellow melting point of silicon and the solubility decreases (sometimes even by an order of magnitude) during cooling which has significant importance for crystallization refining of silicon.

## GERMANIUM

Used **in high-frequency semiconductive components** (has much higher charge carrier mobility than Si – see Table 6.3). Germanium diodes and transistors exhibit high residual current and, considering the production technology, also wide scatter of attributes. The charge carrier mobility in germanium is higher than in silicon - Ge is thus suitable for components operated at high frequencies. In future, processors operated at several hundreds of GHz will be probably developed; their chips will be produced from **germanium and silicon alloy**.

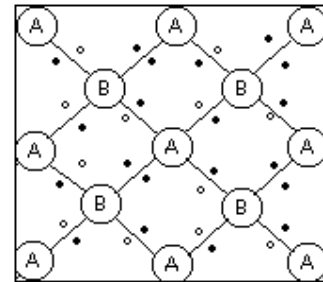
## 6.3.2 COMPOUND SEMICONDUCTOR

### 6.3.2.1 Compounds of A<sup>III</sup>B<sup>V</sup> type

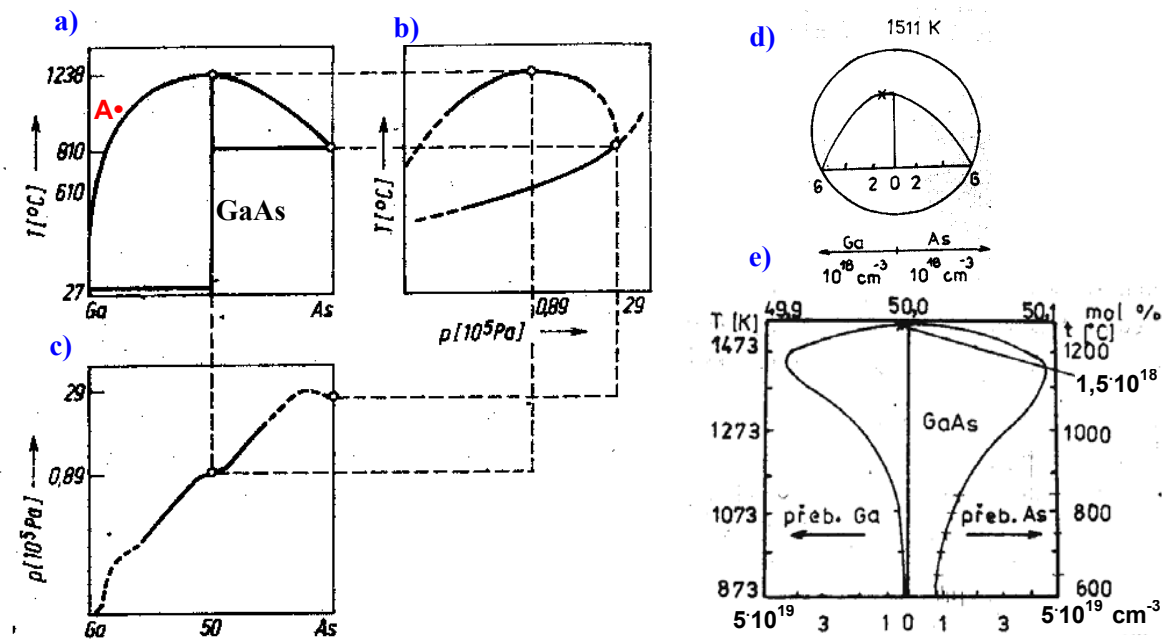
These materials have predominantly covalent inter-atomic bonds with favorable semiconducting properties. Atoms of III. and V. group, placed in the nodes of diamond lattice, form A<sup>III</sup>B<sup>V</sup> type semiconductor – Table 6.4.

**Table 6.4** Production possibilities of A<sup>III</sup>B<sup>V</sup> type compounds

| III/V | N   | P          | As              | Sb               |
|-------|-----|------------|-----------------|------------------|
| B     | BN  | BP         | BA <sub>s</sub> | BS <sub>b</sub>  |
| Al    | AlN | AlP        | AlAs            | AlS <sub>b</sub> |
| Ga    | GaN | <b>GaP</b> | <b>GaAs</b>     | GaS <sub>b</sub> |
| In    | InN | InP        | InAs            | InS <sub>b</sub> |



**Fig. 6.5** Covalent bond character of A<sup>III</sup>B<sup>V</sup> compounds



**Fig. 6.6**  $p - T - X$  equilibrium phase diagram of Ga – As system

a) Diagram  $T - X$ ; b) Diagram  $p - T$  (upper curve – vapor pressure of As in compound at temperature of a liquid; lower curve – vapor pressure of pure arsenic); c) Diagram  $p - X$  (As vapor pressure in relation to As concentration corresponds to curves of a liquid); d) Detail of stoichiometric region in vicinity of congruent melting point of GaAs ( $T_m = 1238^\circ\text{C}$ ). e) Retrograde character of solid phase is evident on both the Ga and As side in GaAs stoichiometric composition.

Ternary compounds of A<sup>III</sup>B<sup>V</sup> type -  $\text{Ga}_{1-x}\text{Al}_x\text{As}$  (laser diodes LD)  
 -  $\text{GaAs}_{1-x}\text{P}_x$  (light emitting diode LED)

N-type non-intrinsic conductivity – II. group elements – acceptors (doped with Zn).

P-type non-intrinsic conductivity – V. group elements – donors (doped with Se, Te).

A<sup>III</sup>B<sup>V</sup>  $\Delta W = 0.2 \div 2.3$  eV (wide band gap) – see Table 6.3.

wide  $\Delta W$   $\Rightarrow$  diodes and transistors for operating temperatures higher than Si,  
narrow  $\Delta W$   $\Rightarrow$  photoelectric compounds for infrared region.

Semiconductor quality cannot be assessed by chemical analytic methods. Basic criterion is **resistivity, conductivity type, mobility and lifetime of charge carriers**. Another requirement is stress-free and low-defect structure of semiconductor single crystals. **Single crystals** are prepared in certain crystallographic plane, orientation of crystal axis is usually  $\langle 111 \rangle$  or  $\langle 100 \rangle$ .

Dopant atoms behavior in semiconductive  $A^{III}B^V$  compounds corresponds to its location in the periodic table. **Second group elements** can replace the A atoms in crystalline lattice of  $A^{III}B^V$  compounds and thus act like **acceptors**. **Sixth group elements** can replace the B atoms thus forming **donor centers**. **Fourth group elements** can replace both the A and B atoms in  $A^{III}B^V$  compound and therefore have **amphoteric** character. Typical acceptor additives are Cd and Zn, donor additives are usually Se and Te. However oxygen in all  $A^{III}B^V$  compounds forms deep additive levels.

From purely technological point of view, the  $A^{III}B^V$  compounds can be divided in three groups:

1. compounds with low vapor pressure at the melting point - InSb, GaSb, AlSb,
2. compounds with higher vapor pressure at the melting point - InAs, GaAs, InP, GaP,
3. compounds with high melting point and corresponding high vapor pressure - AlAs, BP, AlN.

Synthesis methods for semiconductive  $A^{III}B^V$  compounds and simultaneously crystal preparation methods are based on knowledge of  $p - T - X$  (pressure – temperature – composition) equilibrium phase diagrams. Phase diagrams are very similar for all  $A^{III}B^V$  type compounds. Typical example is shown in Fig. 6.6:  $p - T - X$  phase diagram for gallium arsenide.

As it was shown in previous example, all binary  $A^{III}B^V$  systems behave similarly and form one congruent melting stoichiometric compound of AB type. AB compounds exhibit certain minimal solubility of both A and B element with deviation to both sides – see the detail from stoichiometric region composition of GaAs compound near melting point – Fig. 6.6 e). Three dimensional phase diagram with (pressure – temperature – composition) must be utilized for synthesis and other technological operations of semiconductive compounds – see Fig. 6.6.  $A^{III}B^V$  synthesis methods are divided to:

**A) synthesis from stoichiometric liquid**

- a) at normal pressure (for compounds with low vapor pressure at the melting point);
- b) at elevated, resp. high vapor pressure corresponding to the crystallization temperature, i.e. to the dissociation pressure of the compound in the liquid.

**B) synthesis from non-stoichiometric liquid** (see **point A** in Fig. 6.6 a).

**D) synthesis utilizing chemical deposition of vapor** of individual components. Mostly used for epitaxy of  $A^{III}B^V$  layer production.

**E) synthesis with simultaneous condensation of pure component vapors by MBE method** (Molecular Beam Epitaxy) – utilized for production of epitaxy layers.

**F) SSD synthesis method (Synthesis – Solution – Diffusion).**

Production of semiconductive  $A^{III}B^V$ ,  $A^{II}B^{VI}$  compounds with high vapor pressure (GaAs, InAs, CdTe,  $Cd_xHg_{1-x}Te$ )

- Higher pressure melting. Gas pressure must correspond to the dissociation pressure of the liquid.
- The temperature of the recipient must be higher than the condensation temperature of volatile compound.
- Melting in quartz ampoules.
- Excess of the volatile (As, P, Cd, Zn...) component outside the reaction chamber – compensation of their evaporation from the melt liquid of  $A^{III}B^V$  or  $A^{II}B^{VI}$  which have high melting point well above melting point of the basic elements.

Preparation of single crystals under boron oxide liquid is a significant improvement. It is referred to as **LEC (Liquid Encapsulated Czochralski)**.

GaAs, PbTe, PbSe single crystal preparation - shielded with melt  $B_2O_3$ .

**$B_2O_3$  properties:** hygroscopic (necessary to anneal at 600 °C and normal pressure and then at 1000 °C in vacuum), the enamel is transparent. For higher temperatures, CaO, BaO,  $CaCl_2$ ,  $BaCl_2$ , KCl and others are used.

Fabrication of semiconductive compounds at high pressure in autoclave (GaP)

The production technology of semiconductive compounds, single crystals and single crystal epitaxy layers is at very advanced level. This broadens the application variety of these compounds for production of new types of

electronic, microelectronic and optoelectronic parts. Table 6.5 presents overview of typical  $A^{III}B^V$  compounds and their application.

**Table 6.5** Overview of  $A^{III}B^V$  compound applications

| Compound   | Application  | Physical phenomenon                                  |
|--|--|--|
| GaAs, InP, $In_xGa_{1-x}As$  | Hf. transistors and MIC                              | High electron mobility                               |
| GaAs, InP  | Hf. generators and amplifiers, Gunn diodes           | Gunn phenomenon                                      |
| GaAs   | Hf. generators and amplifiers                        | Cascade effect                                       |
| GaAs   | Frequency multipliers, parametric amplifiers, tuning | Voltage dependency of PN transition capacity         |
| GaAs   | Electro-acoustic amplifiers, signal delay circuits   | Piezoelectric effect                                 |
| GaAs, $GaAs_xP_{1-x}$ , $Al_xGa_{1-x}As$ , GaP, $(In,Ga)(As,P)$                      | Luminescence diodes                                  | Recombination of carriers on PN transients emits ray |
| GaAs, $GaAs_xP_{1-x}$ , $In_xGa_{1-x}As$ , $Al_xGa_{1-x}As$ , $(In,Ga)(As,P)$ , InSb | Radiation detectors                                  | Generation of pair on PN transient emits ray         |
| GaAs, $Al_xGa_{1-x}As$ , $(In,Ga)(As,P)$   | Coherent light sources (laser diodes)                | Recombination of carriers by injection               |

Note: Hf. – high frequency, MIC – monolithic integrated circuits

## Overview of important $A^{III}B^V$ compounds

### BORON COMPOUNDS

- a) **BN** – Hexagonal lattice (soft, high resistivity), cubic lattice (diamond-like hardness, oxidation at 2000 °C, stable in vacuum up to 2700 °C, does not dissolve in acids).  
Application – crystallizers for synthesis and preparation of single crystals of various semiconductive compounds.
- b) **BP** – sfalerite structure, transparent crystals  
Properties and application – current rectification properties up to 400 °C.

### ALUMINUM COMPOUNDS

- a) **AlN** – colorless crystals.  
AlN properties:  $N_2$  evaporates at  $T > 2000$  °C, dissociation in vacuum at 1750 °C, oxidation in air at 1200 °C.  
Application: crucibles for  $A^{III}B^V$  preparation.
- b) **AlP** – Properties: mildly soluble in  $H_2O$ , acids and alkalis with  $PH_3$  interaction. Thermally stable up to 1000 °C.  
Product: pins of AlP (yellow, 1 mm length) – crystallization from non-stoichiometric liquid.  
Application: rectifiers, electroluminescence diodes, photovoltaic cells.
- c) **AlAs** – Properties: grey powder with metallic gloss, well soluble in  $H_2O$ , reacts with atmosphere humidity.  
Preparation: from powders in  $SiO_2$  ampoule or from gas.
- d) **AlSb** – Properties: grey powder with metallic gloss, pure AlSb is stable in air.  
Application: solar cells, diodes.

### GALIUM COMPOUNDS

- a) **GaN** – Properties: low solubility in acids and alkalis, oxidation in air at 1000 °C.  
Application: epitaxial layers of GaN – luminescence blue-light diodes, complex luminescence devices, colored imaging components.

- b) **GaP** – Properties: sfalerite structure, high chemical stability (no reaction with air O<sub>2</sub> up to 700 to 800 °C), band gap width  $\Delta W = 2.25$  eV, melt GaP interacts with the crucible material (highly pure graphite or quartz is suitable) – danger of contamination.  
Application: diodes, luminescence components in visible spectrum – emits red or green light depending on the diffused material.
- c) **GaAs** – Properties: does not react with water, poisonous AsH<sub>3</sub> is formed by reaction with acids. Does not oxidize up to 300 °C, decomposes at 600 °C. Melt GaAs is highly reactive. High mobility of charge carriers. Lattice parameters of GaAs and Ge are very similar (epitaxy of GaAs on Ge and opposite).  
Application: laser diodes, hf. devices (tunnel diodes, MESA diodes, MOS transistors, opto-transistors, solid regulation circuits, switching of power circuits).  
**GaAs<sub>1-x</sub>P<sub>x</sub>**, for x = 0.45 (**red diodes**); for x = 0.9 (**yellow diodes**). Epitaxy GaCl<sub>3</sub>, AsH<sub>3</sub>, PH<sub>3</sub>.
- d) **GaSb** – Properties: sfalerite structure, cleavage plane (110), alloyed with Se, Te: N-type.  
Application: laser diodes ( $\lambda = 1.6$  μm), low-noise hf. diodes.

### INDIUM COMPOUNDS

- a) **InP** - Properties: dark grey crystals, metallic gloss, cleavage plane (110).  
Application: laser diodes.
- b) **InAs** – similar properties as InP.
- c) **InSb** - Properties: exceptional electron mobility, low vapor pressure of the components.  
Application: Hall generators, laser diodes (5.2 μm) - InSb<sub>x</sub>As<sub>1-x</sub>, laser diodes emitting light of specific wavelength.

**Compounds with heterogeneous structure** (quaternary semiconductive compounds) on, e.g. InAs/GaSb/AlSb basis, have significant importance for optoelectronic devices, because they have similar lattice. The band gap and conduction band width can be adjusted by changing the element ratios.

### 6.3.2.2 A<sup>II</sup>B<sup>VI</sup> compounds - chalcogenides

Table 6.6 Overview of A<sup>II</sup>B<sup>VI</sup> compounds

| II/VI | O   | S   | Se   | Te   |
|-------|-----|-----|------|------|
| Zn    | ZnO | ZnS | ZnSe | ZnTe |
| Cd    |     | CdS | CdSe | CdTe |
| Hg    |     |     | HgSe | HgTe |

Other combinations:

Cd<sub>x</sub>Hg<sub>1-x</sub>Te,  
Cd<sub>x</sub>Zn<sub>1-x</sub>Te,  
CdTe<sub>x</sub>Se<sub>1-x</sub>,  
CdTe<sub>x</sub>S<sub>1-x</sub>.

- Properties**: Dominantly ionic bond character at the expense of covalent and with some portion of metallic bond.
- Application**: Optoelectronic components as light detector, solar cells ...  
CdS, CdSe – **photo-resistors**, **photo-diodes**  
ZnS – **cathode-luminescence components** – e.g. (Zn,Cd)S:Ag  
ZnS, ZnSe – **electro-luminescence displays**  
CdTe, HgSe, Cd<sub>x</sub>Hg<sub>1-x</sub>Te, CdTe<sub>x</sub>Se<sub>1-x</sub> – radiation in wide wavelength range - **photodetectors**, e.g. **roentgen and nuclear γ-ray detectors**, **ultraviolet** and **infrared spectrum** detectors, **thermoelectric generators**.

### 6.3.2.3 A<sup>I</sup>B<sup>VII</sup> compounds

**Examples**: **CuCl, CuBr, CuI, AgI, NaI.**

**Properties**: Interesting photoelectric and thermoelectric properties, predominantly ionic bond character, wide band gap  $\Delta W = 2.94$  eV for CuBr; 2.8 eV for AgI.

**Application**: **Scintillation detectors for nuclear radiation.**

### 6.3.2.4 A<sup>IV</sup>B<sup>VI</sup> compounds

**Examples**: **GeTe, SnTe, PbS, PbSe, PbTe.**



**Properties:** Specific photoelectric and thermoelectric properties, GeTe – superconductive at low temperatures.

**Application:** PbS, PbSe, PbTe,  $Pb_{1-x}Sn_xTe$  – **infrared light detectors**.  
 $Pb_{1-x}Sn_xTe$  – **photo-diodes** operating up to 1 GHz frequency.  
PbS – **photo-resistors**.

$Pb_{0,8}Sn_{0,2}Te$ , PbTe – integrated infrared detectors (wavelength 3 to 14  $\mu m$ ), CCD cameras.  
All compound types – injection laser diode emitting in infrared spectrum.

### 9.3.2.5 $A_3^{II}B_2^V$ compounds

**Examples:**  **$Cd_3As_2$ ,  $Cd_3P_2$ ,  $Zn_3As_2$ ,  $Zn_3P_2$** .

**Application:** **Photovoltaic and solar cells**, Schottky diodes, **photoluminescence diodes** and lasers.

### 6.3.2.6 $A_2^VB_3^{VI}$ and $A_2^{III}B_3^{VI}$ compounds

**Examples:**  **$Bi_2Te_3$ ,  $Bi_2Se_3$ ,  $Sb_2Te_3$ ,  $In_2Te_3$** .

**Application:** **Thermoelectric generators** – direct conversion of electricity to heat and the opposite, temperature stabilizers, air-conditioning, coolers.

### 6.3.2.7 $A^{IV}B^{IV}$ compounds

**Example:** **Ge-Si**

**Properties:** Ge and Si have ideal binary diagram and are completely soluble in both liquid and solid state.  
Substitution of the Si by Ge changes the  $\Delta W$  and charge carrier, but significantly decreases the thermal conductivity

**Application:** **High-temperature thermoelectric materials**, diodes, transistors and photo-detectors for **infrared** spectrum

**Example:** **Silicon carbide SiC**

**Properties:**  $T_m = 2600$  °C,  $\Delta W = 2.8$  eV, electron emission during the P-N transient.

**Application:** optoelectronics, **blue luminescence diodes**, transistors, high-temperature diodes.

### 6.3.2.8 Special semiconductive compounds

**Examples:**  **$Si_3N_4$** .

**Properties:** **Dielectric compound**, wide band gap  $\Delta W = 4.5$  eV at  $T = 300$  K, resistivity at 300 K is  $\rho = 10^{15} \div 10^{16}$   $\Omega \cdot cm$ .

**Application:** Passivation layers for integrated circuits produced by planar-epitaxial technology.

### 6.3.2.9 Oxide semiconductive compounds

**Properties:** Bond between atoms is both covalent and ionic, presence of metallic ions of various valence, non-stoichiometric ratio of atoms in the compound. Transition metal of the 4. period oxides: Ti, Mn, Fe, Co without fully populated sub-layer 3d exhibit good semiconductive properties. These materials have polycrystalline structure, band gap width is usually  $\Delta W > 2$  eV.

**Ferrites:**  **$Fe_2O_3 + (TiO_2, NiO, ZnO, CuO, MnO, PbO, SrO \dots)$**

**Application:** both ferromagnetic hard and soft materials – see chapter 4, **thermistors** – characteristic thermal dependency of resistance.

**Ferroelectrics:**  **$TiO_2 + (oxides La, Nb, Ta, Ba, \dots)$  e.g.  $SrO \cdot TiO_2$ ,  $PbO \cdot TiO_2$ ,  $BaO \cdot SnO_2$ ,  $CaO \cdot SnO_2$ ,  $CrO \cdot SnO_2$ ,  $MgO \cdot ZrO_2$**

**Application:** ferroelectric and piezoelectric materials – see chap. 7, **PTC thermistors** (positive temperature coefficient).

**Garnets:**  **$Ln_3Fe_5O_{12}$** , where Ln is suitable lanthanide, e.g. Gd, Sm, Eu, Tb (with the exception of Nd, Pr, La and Ce) or yttrium – e.g. garnets of GGG type  **$Gd_3Ga_5O_{12}$** , YIG type garnets  **$Y_3Fe_5O_{12}$**  or YAG garnets  **$Y_3Al_5O_{12}$** .

- Properties:** Isotropic magnetic materials with low magnetization and high mobility of cylindrical domains „bubbles”. This phenomenon is intensively utilized in, for example, memory modules. The magnetic layer must have minimum defects (dislocations, impurities, cracks, magnetic dust).
- Production:**  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$  (melting point  $T_m = 1850\text{ }^\circ\text{C}$ ) produced from gadolinium oxides and gallium of 4N purity
- Application:** **bubble memory material** for superfast computers.

### 6.3.2.10 Simple oxide semiconductive compounds

- Examples:**  $\text{ZnO}$ ,  $\text{TiO}_2$
- Application:** **voltage-independent resistors.**

**Quartz:**  $\text{SiO}_2$

- Properties:** Dielectric compound, wide band gap  $\Delta W = 8\text{ eV}$  and  $\rho = 10^{15} \div 10^{16}\text{ }\Omega\cdot\text{cm}$  at 300 K.
- Application:** **Dielectric and insulation layer** for fabrication of integrated circuits, quartz tubes, crucibles for Si melting, diffusion processes, epitaxy, light guides.

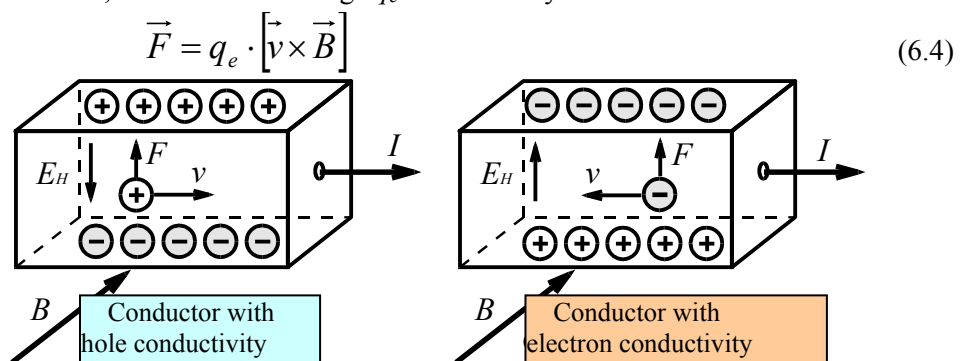
**Sapphire:**  $\text{Al}_2\text{O}_3$

- Properties:** Dielectric compound, wide band gap  $\Delta W = 5\text{ eV}$ ,  $\rho = 10^{15} \div 10^{16}\text{ }\Omega\cdot\text{cm}$  at 300 K, melting point of  $T_m = 2050\text{ }^\circ\text{C}$ , modification:  $\alpha\text{-Al}_2\text{O}_3$  – hexagonal,  $\gamma\text{-Al}_2\text{O}_3$  – cubic.

- Application:** **Dielectric substrates** for silicon epitaxial layers preparation, various applications in optoelectronics.

## 6.4 HALL EFFECT

Thin, rectangular semiconductive or conductive plate with current flowing through it is put into magnetic field of induction  $B$  (Fig. 6.7). In this field, force  $F$  on the charge  $q_e$  with velocity  $v$  is:



**Fig. 6.7** Principle of Hall effect and determination of conductivity type in semiconductive materials

Force  $F$  bends the charged particles trajectories in such manner, that opposite charges are generated on the opposite sides of the plate and transverse voltage  $E_H$  is generated. Direction of  $E_H$  depends on the type of predominating charge carrier, i.e. semiconductor type (Fig. 6.7). Deviation of the charge carriers continues until the generated electric field  $E_H$  compensates the effect of the magnetic field. Then, the force  $F$  which is applied to the charge by the electric field, is equal to the Lorentz force and the system reaches equilibrium, because the total force on the charge moving through the plate is zero.

This so called **Hall voltage**  $U_H = E_H d$  measured between the top and the bottom side of the plate can be described by equation:

$$U_H = R_H \frac{I B}{d}; \quad R_H = \frac{1}{N q_e}, \quad (6.5)$$

$I$ ,  $B$ ,  $q_e$  have been used previously,  $d$  is the thickness of the plate and  $N$  is the concentration of free charge carriers in measured sample. Attribute  $R_H$  ( $\text{m}^3 \cdot \text{C}^{-1}$ ) is called **Hall coefficient**. Sample with positive charge carriers (hole conductivity) has  $R_H > 0$ , sample with electron conductivity has  $R_H < 0$ .

Voltage  $U_H$  is reciprocal to the difference of major and minor charge carrier concentration. This is because electron and a hole have opposite electric charge. Magnetic field has opposite effect on holes and electrons and deflects them to opposite sides. Holes and electrons also move in opposite direction in electric field. If the concentration of holes and electrons is the same, the effect of Hall phenomenon is zero.

## 6.4.1 Application of Hall effect

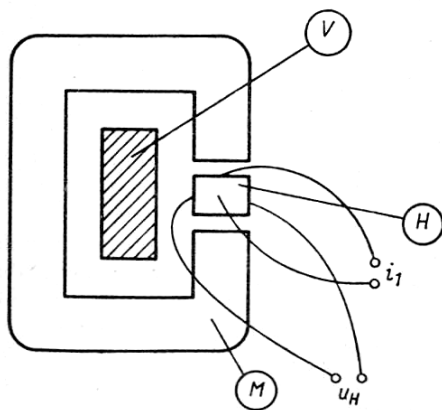
In practice, Hall effect is utilized mostly in devices for magnetic induction measurement, for construction of multipliers and modulators and for measurement of physical attributes of semiconductors.

**Hall effect sensor:** semiconductive components for magnetic field measurements. Semiconductors (e.g. GaAs, Si, InSb) subjected to magnetic field and electrical current flowing perpendicularly to the magnetic field, a voltage, perpendicular to both magnetic and electric field, is generated on the contacts of the semiconductor. Hall sensor is required to have the highest possible Hall coefficient  $R_H$ . This is met by a semiconductor with high concentration of major charge carriers. Hall sensor then must generate high enough voltage  $U_H$ . Hall coefficient and resistivity must be very low temperature-dependent. These requirements are best matched by **semiconductor of A<sup>III</sup>B<sup>V</sup> type**.

Hall sensor comprises of semiconductive plate with four electrodes attached. Two electrodes are terminals for current source connection and the other two for Hall voltage sensing. The thickness of semiconductive plate is usually around 0.1 mm. It must be placed in protective casing to prevent mechanical damage.

### Application of Hall sensor

The measuring current is held at constant value and magnetic induction is measured.



Automatization and regulation – measurement of direct current passing through the conductor. The probe with hall effect sensor **H** for current measurement is placed in the magnetic field (Fig. 6.8). Current flows through conductor **V**, passes through the iron core **M**, thus creating a magnetic circuit. Hall effect sensor **H** is placed to the gap of the magnetic circuit. The output voltage from Hall effect sensor is reciprocal to the current level passing through the conductor, is „non-alternating”, and its polarity depends on the current flow direction.

Fig. 6.8 Measurements of DC voltage using Hall effect sensor

Alternating current, even high-frequency current, passing through Hall sensor can be altered by changing the magnetic field; altered voltage can be collected as alternating Hall voltage. This configuration is called **Hall moduler**.

**Hall sensors** can be utilized for mathematical operations (multiplication) and for low-frequency current generation or as components of electronic switches controlled by magnetic field.

**Small ventilators**

**Distance measurement**

**Other applications:** various proximity, safety, water level and pressure switches and others.

## 6.5 INTEGRATED CIRCUIT PRODUCTION TECHNOLOGY

### 6.5.1 Fabrication and modification of Si wafers

For production of semiconductive components, single crystal material, in form of small, 150 to 400  $\mu\text{m}$  thick wafers with planar, high-quality, mirror-like surface of defined crystallographic orientation is used. Precise dimensions are also required in many cases – **see Power Point presentation „From silica to silicon wafer”**.

**Raw material:** single crystal silicon produced by Czochralski or zone melting method – cylindrical body of 100 to 300 mm diameter, 200 cm length, and 50 to 300 kg weight with crystallographic orientation usually being  $\langle 111 \rangle$  or  $\langle 100 \rangle$  with  $1^\circ$  precision. **Crystallographic orientation** is examined by roentgen or optic method right after the

single crystal fabrication process is finished. **Resistivity of the crystal** also needs to be measured in both axial and radial direction which is carried out by 4-point method by automatic device with PC data output.

### 1. STEP– Grinding of Si crystal to desired diameter

Rod of single crystal Si has never precise diameter along its length. The adjustment to cylindrical shape of desired diameter is facilitated by grinding on centre-less grinding machine. During centre-less grinding, the single crystal rod lies on support ruler and is moved by the grinding disc without the necessity of being held or centered; the ground piece is rotating along its axis. The movement of the work piece needs to be slowed down relative to the grinding disc and held at this speed by feed roll which is rotating in the same direction as the grinding disc (with diamond suspension on its surface), but slower.

### 2. STEP – facets grinding on Si crystal

One to four parallel planes - facets are ground on every crystal. These are used to determine the position of Si wafer in the device (main facet) and identification of orientation or type of conductivity (auxiliary facet) – Fig. 6.9. Main facet is always longer than the auxiliary. There can also be third or fourth facet.

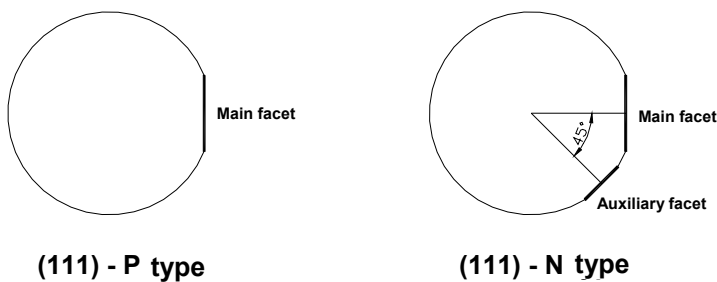


Fig. 6.9 Type of facets on Si wafer

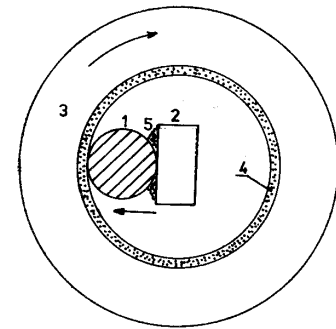


Fig. 6.10 Cutting of Si plates

1 – single crystal, 2 – ceramic pad, 3 – cutting disc, 4 – diamond grain, 5 - cement

### 3. STEP – Slicing the Si single crystal

Several attributes are of importance when choosing suitable method of slicing of cylindrical single crystals: the slicing width (losses – up to one half of the material), slicing speed, complexity and price of the device and the slicing disc, surface quality of the product (wafers).

Three basic methods are being utilized:

- Cutting by circular saw with diamond grain – Fig. 6.10.
- Cutting by belt saw with grinding suspension.
- Cutting by wire saw with grinding suspension.

Cutting by circular ring-shape saw is nowadays the most common method (Fig. 6.10). The cutting tool is fixed on the outer rim, diamond grain is deposited on the inner rim. The tool vibration is thus minimized. The thickness of the tool is  $< 0.2$  mm. Single crystal is agglutinated on ceramic pad. The cutting is facilitated by the diamond saw, the cutting speed is about 1 mm/s; the cut must be water-cooled. It takes about 100 s to cut one wafer with 100 mm diameter.

### 4. STEP – Grinding of the Si wafers

The surface of the Si wafers is very rough and damaged by cutting. The wafers are thus ground on both sides. The goal is to achieve fine, flat, highly planparallel surface on both sides while maintaining the desired thickness. Basic part of the grinding machine is flat grinding disc fixed on vertical arbor. The grinding suspension is fed on the surface of the rotating grinding disc. The wafers are pressed against the working table. The grinding speed and pressure are relatively high (cca 200 RPM and cca  $10^4$  Pa). Grinding powder can be either diamond, corundum ( $Al_2O_3$ ), silicon carbide (SiC) or boron carbide. SiC is typically used for grinding of silicon.

### 6. STEP – Grinding of the Si wafers sides

The sides are rounded by grinding to remove the places tending to chip during integrated circuit production.

### 6. STEP – Cleaning the surface of Si wafers by etching

Etching by nitric acid  $HNO_3$  and hydrofluoric acid HF mixture dissolves impurities and damaged areas of Si wafers.

### 7. STEP – Polishing of Si wafers

Only one side of the wafer is polished. The goal here is to achieve mirror-like finish without scratches or any other flaws. Polishing is realized by very fine aluminum oxide  $Al_2O_3$  powder polishing paste. **Silicon wafer** is thus produced.

### 8. STEP – Final cleaning of Si wafers

The purpose of this step is to remove organic compounds, dust particles and heavy metals from the surface of the Si wafer. The cleaning bath composition is usually:

- a) hydrogen peroxide  $H_2O_2$  and hydrochloric acid HCl,
- b) hydrogen peroxide  $H_2O_2$  and ammonium hydroxide  $NH_4OH$ .

Cleaning solution residues are removed in very clean water, called **demineralized water**.

## **6.5.2 Planar epitaxial technology of integrated circuit production**

### **Characteristics and requirements:**

- 1) high demands on production environment: maintaining required temperature and humidity, dust free,
- 2) necessity of complex and expensive technological equipment,
- 3) highly pure materials and substances are required,
- 4) almost zero repairability,
- 5) high quality and reliability control (due to large number of production steps).

### **Integrated circuit design:**

- 1) circuit design – functions and parameters,
- 2) morphology draft,
- 3) topology design – placement of components and functional blocks on the wafer with regard to:
  - a) mutual thermal interaction of individual components,
  - b) optimal link and maximum efficiency of the chip,
- 4) detail drawing of all motives (by computer) represents optimization of components placement so that the space of the chip is utilized to its maximum,
- 5) correct connection control (manually – visually), control of construction rules and completeness of the data.

Product of the circuit design is a photo mask.

### **Production procedure of transistors and integrated circuits**

- 1) Default substrate Si – e.g. P-type.
- 2) Diffusion of buried layer (by arsenic) – purpose of buried layer is reduction of el. resistance of the collector.
- 3) Epitaxy of N-type layer, 20  $\mu m$  thickness. All active elements of the transistor will be placed here.
- 3) Photolithography and production of insulation layer – diffusion of  $P^{++}$  - reaches the substrate, thus forming isolated islands on epitaxial layer of the Si wafer.
- 4) Photolithography and diffusion – preparation of base space.
- 5) Photolithography and diffusion – production of emitter and collector space – preparation of ohmic contact.
- 6) Preparation of  $SiO_2$  layer and contact windows.
- 7) Photolithography and conductive layer deposition, subsequently shaping of aluminum metallization.
- 8) Measurement and testing of electrical parameters of individual transistors, as well as of the whole circuit.

### **Production procedure of low-power NPN transistor:**

**Epitaxy of Si wafers:** VPE method is usually utilized for Si – [see Chapter 5 and Power Point presentation „Epitaxy”](#).

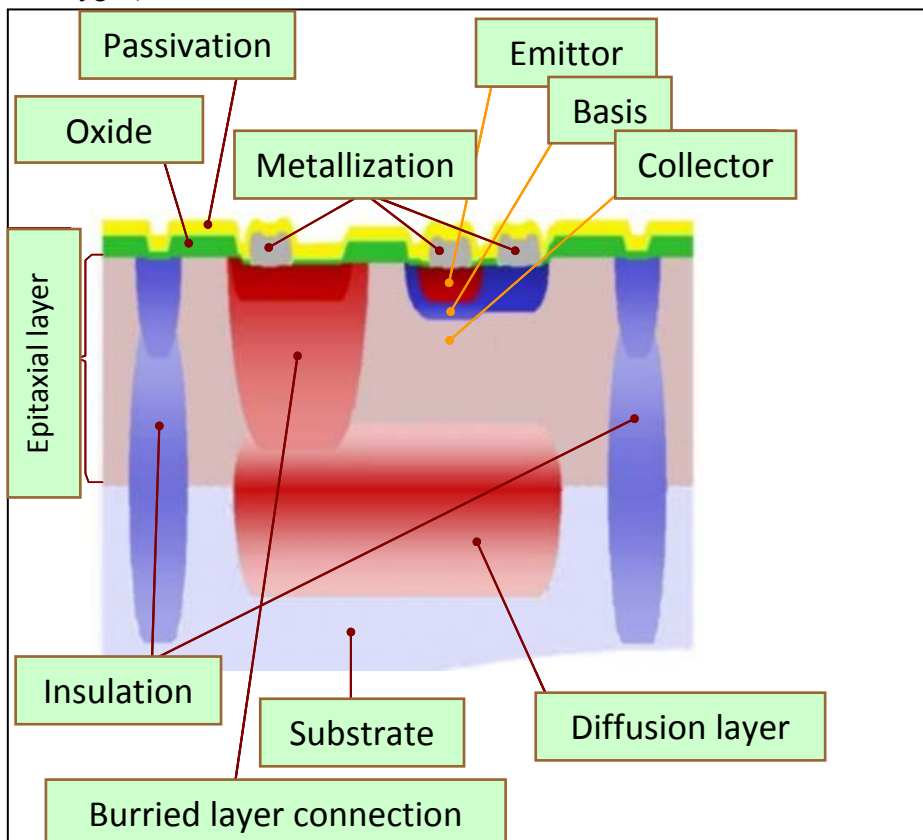
**Oxidation of Si wafers:** Product of Si wafer oxidation is a layer of amorphous silicon oxide  $SiO_2$ . This layer forms on both front (glossy) and back (matt) side of the Si wafer. Oxidation is carried out at high temperatures (900-1200  $^{\circ}C$ ) and is easy to control. Thickness of produced  $SiO_2$  can be in interval of 0.01 to 1  $\mu m$ .

**Photolithography – principle:** photo-resist varnish which can be „hardened” by UV light (mercury gas discharge lamp). Hardening renders the varnish resistant against certain organic thinners, while the non-irradiated varnish dissolves. The photo-resist is also stable in some etchants.

**Technological process:** Si wafer is covered with a thin layer of photo-resist which is hardened by heating at elevated temperature. Then, a mask is placed on the wafer — the mask is produced by fine photographic technique; it is transparent only in places defined by the future circuit layout. The matrix is then irradiated through this photo-resistant layer and the layer is removed from the unexposed area. The wafer is then etched; Si or  $SiO_2$  is dissolved only at unprotected (by hardened photo-resist) areas. The surface is dissolved up to the epitaxial layer, and then, diffusion or metallization layer are produced.

**Diffusion:** The purpose of diffusion is formation of regions with the other type of conductivity and with defined concentration of electric active charges (electrons or holes). Good electro-insulating properties of  $SiO_2$  layer aid to prevent uncontrolled diffusion of the agent on the surface of the Si wafer; the diffusion coefficient of the agent in this layer is couple orders of magnitude lower than in silicon. For boron diffusion, thin boron-silicate glass layer is prepared on the surface and during the second step, boron is diffused. For preparation of N-type

region in Si, suitable volatile phosphorus compound ( $\text{POCl}_3$ ,  $\text{P}_2\text{O}_5$ ,  $\text{PCl}_3$ ) in viable transport medium (hydrogen or oxygen) is diffused from a stable source.



**Fig. 6.11** Arrangement of electro-active components of one transistor on integrated circuit.

Horizontal dimensions of the transistor are ( $145 \times 80 \mu\text{m}$ ), vertical dimensions are ( $5$  to  $20 \mu\text{m}$ ). Thickness of the Si wafer (pad) – cca  $340 \mu\text{m}$ .

– see Power Point presentations „Silicon”, „Bipolar technology” and „MG CMOS”.

### Deposition technology of pure elements (B, P, As, Sb) on Si wafer

- Evaporation of additive elements** – about 250 Si wafers are placed in quartz ampoule together with small vessel containing mixture of Si powder and about 1 % of boron. The ampoule is evacuated to about  $10^{-4}$  Pa, then sealed and brought to high temperature. Boron from the Si powder evaporates and is deposited on the Si wafers.
- Ionic implementation.**

### Cutting of Si wafers:

- Grooving with diamond knife blade or diamond disc cutting.
- Breaking on plastic foil.
- Stretching the foil on a hoop.
- Batching – sorting and palletizing.

### Soldering resp. patching of the chip:

Good electric and thermal contact is required, mechanical strength.

Soldering on series of connectors or on metal casings (covar is a suitable material) – connection of the chip to the pad.

Means: gold foil, lead solder alloys (Pb-Ti-Ni-Ag).

Patching – conductive cements.

### Assembly of the connector:

- Thermo-compression:** Utilizes elastic flow of one (or two) material and their mutual diffusion, temperature about  $300 \text{ }^\circ\text{C}$ , temperature of the tip about  $150 \text{ }^\circ\text{C}$ , Al and Au wires with  $\phi 30 \mu\text{m}$ , especially suitable for gold wires, however electrochemical corrosion of Au and Al is of an issue - problem with reliability.
- Ultrasound:** ultrasound generator ( $20 \div 60 \text{ kHz}$ ) is connected to the head, the tip is horizontally vibrated via convertor; removal of the oxide layer along with friction generates enough heat to form thermo-compression joint. Advantages: no electrochemical corrosion, aluminum is cheaper than gold, no need for a heat source.

### Casing: plastic case:

Tabletting of thermosetting polymer.

Silicon rubber for chip protection (injected at  $150 \div 160 \text{ }^\circ\text{C}$  and  $4.5 \div 6 \text{ MPa}$  pressure).

Polymeration 2 to 3 minutes, hardening at  $150 \div 160 \text{ }^\circ\text{C}$ .

Finishing operations: removal of the casing material residues, circuit trimming, connector shaping .

# 7. OPTOELECTRONICS AND SPECIAL MATERIALS

## 7.1 OPTOELECTRONIC SYSTEMS

The optoelectronic (OE) systems are nowadays utilized in telecommunications (media transfer through optic cables), computing, high-power electronics (opto-thyristors), home appliances, etc., and their importance is growing. Their advantages can be quickly summarized by these parameters:

- high information density in optic transfer channel corresponding to the frequency of applied device (up to  $10^{15}$  Hz) and bandwidth (to 100 Gbit/s),
- high interference resistance (the information transfer is facilitated by neutral photons),
- possibility of contact-less joint (perfect electric separation of input and output signal of the transfer device, suitable for high-voltage circuit control),
- simple maintenance of device operated in visible spectra region by visual control of its state, optical indication, screen and so forth.

Fig. 7.1 shows schematic drawing of typical configuration of a simple OE communication system. Input electric signal is adjusted by the encoder to level suitable for the light generator which converts the electric signal to light signal. The generated light is, via the coupler, fed to the corresponding transmission medium, e.g. optic fiber cable. The last component of the OE telecommunication system is light detector which reversely converts the information carried by the optical fiber cable back to electrical signal which is then amplified and eventually decoded by other systems. Similar configuration of OE components with tight optic link is called **optron**.

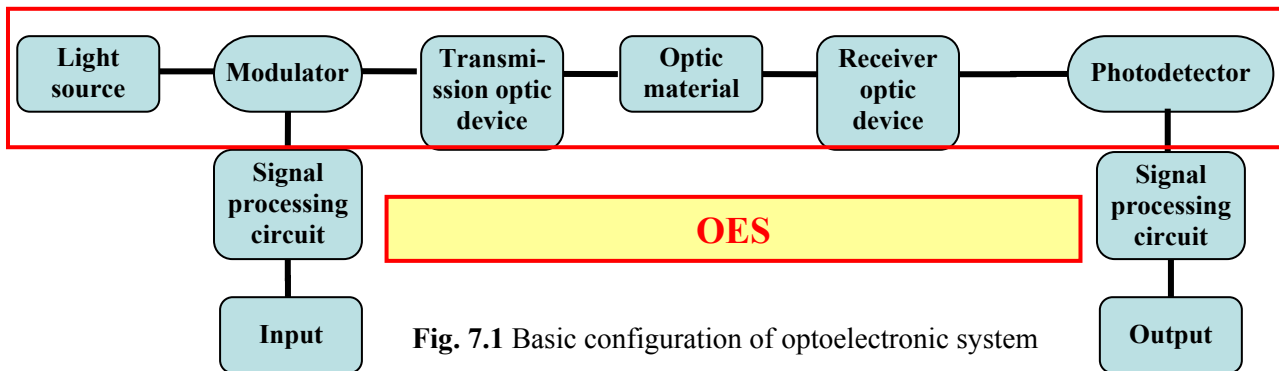


Fig. 7.1 Basic configuration of optoelectronic system

### 7.1.1 Electromagnetic radiation generators

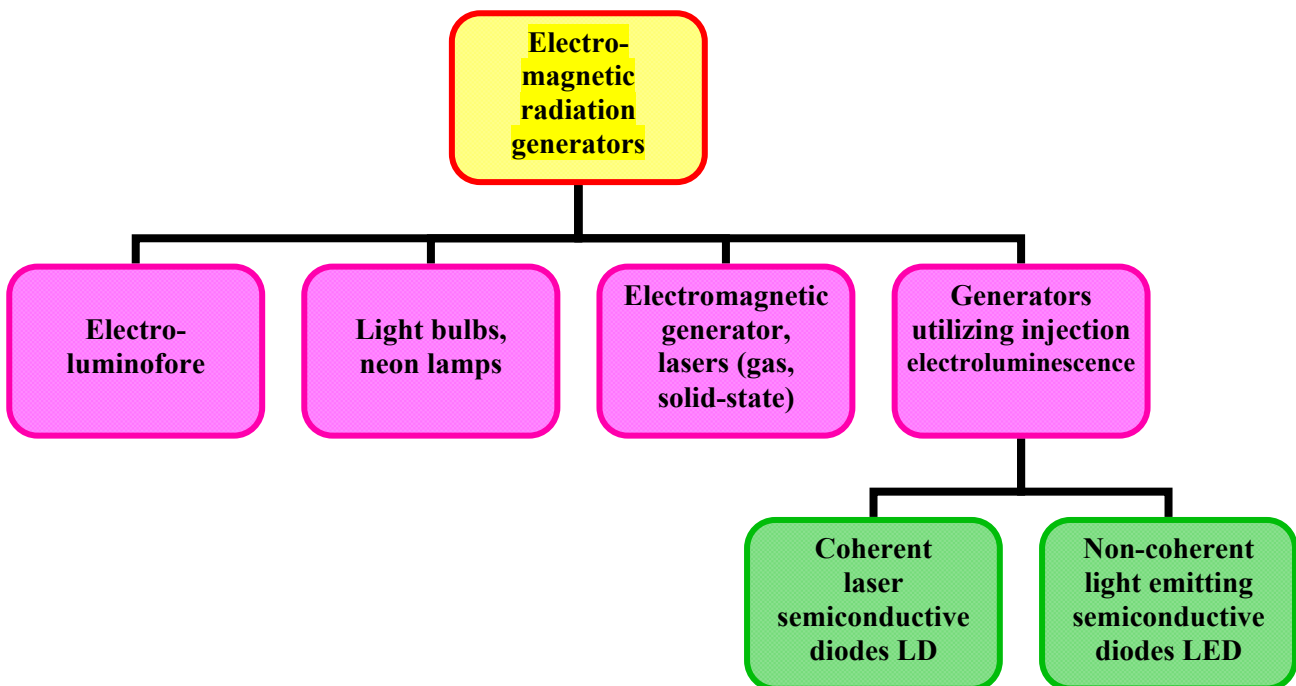


Fig. 7.2 Schematic classification of electromagnetic radiation generators

## Basic types of laser

Lasers distinguished by active medium:

- solid-state,
- liquid,
- gas,
- lasers utilizing charged particle beam.

By pumping mode:

- optical (by vacuum tube, other laser, sunlight, X-ray),
- electrical (collisions in electric field, charged particle beam, electron injection, interaction of electromagnetic field with cluster of charged particles),
- chemically (by chemical bond energy, photochemical dissociation, exchange of energy between molecules and atoms),
- thermodynamically (heating or cooling of gas),
- nuclear energy (reactor, nuclear explosion).

By emitted light wavelength:

- infrared,
- visible light lasers,
- ultraviolet,
- X-ray.

By application:

- scientific,
- measurement,
- medical,
- technological,
- power plant industry,
- military.

By the work regime: **continuous** or **pulse** lasers.

### **a) Solid state lasers**

**Ruby laser** – active medium is corundum crystals ( $\text{Al}_2\text{O}_3$ ) with chromium addition which is the active compound. Irradiation the crystal by light of sufficient intensity and suitable wavelength, e.g. xenon arc lamp (pulse duration in the order of tenths of millisecond) results in excitation of chromium  $\text{Cr}^{3+}$  ions. An active environment is created inside the crystal, able to amplify the input beam by stimulated emission. The beam is also amplified by spontaneous emission. Ruby crystal is placed between two mirrors. The mirrors are parallel and perpendicular to the crystal axis – photons with trajectory perpendicular to the mirrors are repeatedly reflected. The light spreading along the crystal axis gets immensely amplified. One of the resonator mirrors is partially transparent for the generated light and part of the light thus escapes to the surroundings. **Ruby laser emits red light** and consumes the light from the arc lamp (shorter wavelengths, green region of spectrum). **Elliptic mirrors** are used in modern lasers.

The most common are **neodymium lasers**, with the neodymium ions  $\text{Nd}^{3+}$  dispersed in yttrium-aluminum garnet matrix – Nd:YAG for short. Neodymium ions are excited by optic irradiation. Inside them, the photons are absorbed and emitted in four quantum-level energy system. Laser produces infrared beam of high intensity. **YAG laser** is characteristic for its high efficiency; irradiated with simple light bulb can produce continuous light of hundreds watts intensity. Lately, **YAP lasers** with yttrium-aluminum perovskite crystal are often utilized. Active additive is usually rare earth elements, Cr, Co, Ni or U. These elements emit predominantly red and infrared light. Er:YAG is doped with erbium  $\text{Er}^{3+}$  - produced light of 2.94  $\mu\text{m}$  wavelength has high absorbance in water and body fluids which is utilized in medicine and dental applications.

### **b) Liquid lasers**

Liquid lasers operate with **chelates** of various rare earth elements. Most important part of this group is **pigment lasers**, employing solutions of various organic compounds, e.g. **rhodamine**. **Color center lasers** have crystals with defects which absorb spectral lines corresponding to various colors (KCl crystal with lithium addition).

### **c) Gas lasers**

The active medium is a gas mixture sealed in a cylindrical tube made of special glass. Its inner diameter is usually units to tens of mm, its length can be from several cm to couple meters. Gas lasers are perspective and



massive sources of infrared but even ultraviolet light used in engineering and technology. Gas lasers have high efficiency, conversion of electricity to light is more economical. These lasers work in continual regime.

**Helium-neon laser** generates both red and infrared light. It comprises of glass tube filled with mixture with 5 ÷ 10 parts of He / 1 part of Ne ratio. The pumping is facilitated by high voltage electrical discharge inside the tube with the gas mixture. The helium atoms are excited by the discharge and transfer their energy via collisions to the neon atoms. The tube is placed between the mirrors of the outer resonator. The beam has high frequency stability and low divergence. The helium-neon laser is therefore suitable for production of precise clock, precise rangefinders, telecommunication and geodetic applications.

**Argon laser** emits blue-green light. It is able to generate light of tens of watts intensity in continuous regime; it is suitable for technological applications. **Krypton**, cadmium and **metal vapor** (e.g. copper) lasers have similar properties. **Helium-cadmium** laser emits light of three colors – blue, green and red.

Most powerful of all gas lasers is the **carbon dioxide laser (CO<sub>2</sub> laser)**. Considering the size of the tube, it can generate high-power beam. With tube of 20 mm diameter and 1 m length, the laser produces light of about 50 W output power. High-voltage (1000 to 1700 V, 30 to 50 mA) power source is used for excitation. The laser efficiency exceeds 20 %. CO<sub>2</sub> laser can generate infrared light of several hundreds of output power. **CO<sub>2</sub> lasers** are utilized in welding, drilling of metals, diamond, in melting, military and space applications as well as in research.

**Chemical lasers** utilize the energy of exothermic chain chemical reaction to excite the atoms of active medium, e.g. chlorine and hydrogen or hydrogen and fluorine reaction. Special type of chemical laser utilizes the energy produced by dissociation of molecules by UV light (**photo dissociation laser**) - e.g. iodine laser.

**Nitrogen laser** generates ultraviolet light. **Excimer laser** uses special kind of molecules formed by reaction with inert gases, *excimers*, as an active medium. These molecules can react with highly excited atoms. Ultraviolet light is emitted during dissociation of these molecules. First excimer laser used liquid **xenon** pumped by electron beam. Later excimer lasers use **XeF**, **KrF**, **ArF** molecules as an active medium.

#### d) Semiconductor laser

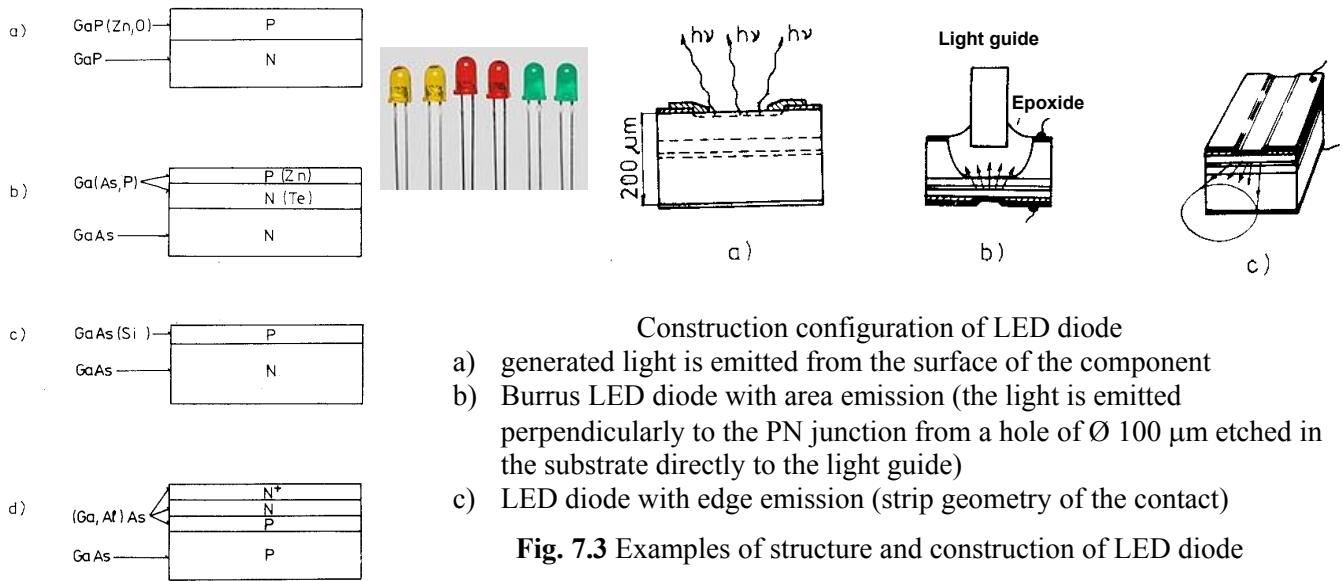
Semiconductor lasers belong to the group of solid state lasers, however they have some special attributes utilized foremost in optoelectronics. First **semiconductor lasers** were of the *injection type*, they utilized the PN junction and used **gallium arsenide (GaAs)** as it has proven to be the most suitable material. Laser emits light of 840 nm wavelength and its power outputs and efficiency strongly depends on operation temperature. Fabrication of structure with *hetero-junctions* had a prime importance in following research of semiconductor lasers. **Al<sub>x</sub>Ga<sub>1-x</sub>As laser** can be operated at room temperature with about 20 % efficiency and 200 mW of continual power throughput. Apart from the injection semiconductor lasers, the *electro-ionization* semiconductor lasers have been put into practice, e.g. on cadmium sulfide crystal. Laser CdS emits green light of high pulse power throughput at room temperature.

**Light emitting diode LED** is a source of **non-coherent light**. Physical principle of LED is **recombination of electron with a hole**. Injection of major charge carriers to semiconductor with the opposite type of conductivity, simultaneously with voltage applied on the PN junction in its forward direction, results in recombination of electron-hole pair and release of the energy quantum of the certain wavelength which can be either directly emitted out of the crystal or absorbed on the lattice, thus increasing its temperature. The emission probability is much higher for a semiconductor with **direct band gap** such as GaAs, in which the minimum of conduction band has the same wavenumber as the maximum of the valence band. The probability increases with wider band gap. For silicon ( $\Delta W = 1.12$  eV) is the emitted energy predominantly absorbed in the crystal (temperature increase) and must be therefore drained via metal or plastic casing. In GaAs ( $\Delta W = 1.423$  eV at 300 K), significant portion of the recombination energy emits in the form of photons of certain wavelength (infrared spectrum). GaAs<sub>x</sub>P<sub>1-x</sub> is produced by partial substitution of arsenic by phosphorus which emits red visible light on the PN junction. Diodes emitting green, yellow or orange light in the forward direction can be fabricated from the material with suitable band gap width  $\Delta W$  (**Ga<sub>x</sub>Al<sub>1-x</sub>As and GaP – red, In<sub>x</sub>Ga<sub>1-x</sub>P – green, SiC - blue**). Diode is connected in its forward direction via suitable resistor to a DC power source. LED diodes are utilized for indication purposes (replacement of unreliable light bulbs), in information screens (seven segment or matrix display) or for car direction lights. Application of luminescence diodes with fitting colors (RGB model) in flat screens is also perspective. LED diode (non-coherent light) predominantly emits spontaneously, the **semiconductor diode LD** (coherent light) mostly by stimulated emission.

#### Semiconductor laser design

The diode structure on Fig. 7.3a) is fabricated on N-**GaP** substrate (thickness about 200÷300 μm). P-type layer prepared by LPE method in flow system is doped by Zn and O forming an iso-electric complex. Melt Zn is alloyed

from gas phase with the help of auxiliary thermal zone of Zn which maintains constant Zn vapor pressure above the melt metal. Sufficient oxygen concentration is ensured by surplus  $\text{Ga}_2\text{O}_3$  in the melt metal. Such diode emits **red light** of 690 nm wavelength and its external quantum efficiency reaches up to 5 %.



**Table 7.1** Materials for LED diodes with various color

|  | Color       | Wavelength                 | Semiconductive material  | Voltage loss |
|--|-------------|----------------------------|--|--------------|
|  | Infrared    | $> 760 \text{ nm}$         | GaAs; $(\text{Al}_x\text{Ga}_{1-x}\text{As})$                                      | 1.6 V        |
|  | Red         | $610 < \lambda < 760$      | AlGaAs; $\text{GaAs}_x\text{P}_{1-x}$ ; (GaP)                                      | 1.8 – 2.1 V  |
|  | Orange      | $590 < \lambda < 610$      | $\text{Ga}_x\text{As}_{1-x}\text{P}$ ; $(\text{Al,Ga,In})\text{P}$ ; GaP           | 2.2 V        |
|  | Yellow      | $570 < \lambda < 590$      | GaAsP; AlGaInP; GaP  | 2.4 V        |
|  | Green       | $500 < \lambda < 570$      | $\text{In}_x\text{Ga}_{1-x}\text{N}$ ; GaN; GaP; $(\text{Al,Ga,In})\text{P}$       | 2.6 V        |
|  | Blue        | $450 < \lambda < 500$      | ZnSe; $\text{In}_x\text{Ga}_{1-x}\text{N}$ ; SiC                                   | 3.0 – 3.5 V  |
|  | Violet      | $400 < \lambda < 450$      | $\text{In}_x\text{Ga}_{1-x}\text{N}$   | 3.0 – 3.5 V  |
|  | Ultraviolet | $\lambda < 400 \text{ nm}$ | diamond (235 nm); BN (215 nm); $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ; AlN (210 nm) | 3.5 V        |

### 7.1.2 Photo-detectors

Photo-detectors are usually terminal components of the OE system. Almost all photo-detectors in OE circuits utilize the **photoelectric** or **photovoltaic effect**. **Free charge carriers** are generated during absorption of light in semiconductor which subsequently increases its **electric conductivity**, or **crystal** increases its **temperature** by absorption which can also increase the conductivity. Photo-detectors are fabricated as components for selected light type (wavelength).

#### Origin of photovoltaic conductivity

- a) Transition of carriers from valence band to conduction band if energy of the absorbed light is higher than  $h \nu > \Delta W$ . This limit is very distinctive in forward transfer semiconductive materials.
- b) Ionization of donor centers. Its low activation energy allows for absorption of light with greater wavelength  $\lambda$ .
- c) The number of free carriers is constant. However the photon energy causes their redistribution on individual energy levels (excited state) and as a result also changes in their mobility. Externally, change in electric conductivity is observed.

#### Photo-detector design

- a) Structure of detector with PN junction. Si diode fabricated by common diffusion technology.
- b) **Silicon PIN diode**. On the substrate plate made of high-ohmic – intrinsic Si,  $\text{N}^+$  layer prepared by epitaxy, thin  $\text{P}^+$  layer by ionic implementation. On top of these layers, a layer of  $\text{SiO}_2$  is produced to reduce the light losses caused by reflection. PIN diodes are characteristic for their high photo-sensitivity (maximum at  $\lambda = 0.9 \mu\text{m}$ ), quick response and adjustability for integrated circuits.
- c) **Photodiodes with heterogeneous structure**. On GaAs plate,  $\text{N}^+$  layer is produced by epitaxy from liquid phase and  $\text{P}^+$  from solid solution of  $\text{Ga}_{0,6}\text{Al}_{0,4}\text{As}$ . This solution has about cca 0.4 eV higher  $\Delta W$  than N layer of GaAs.

(Ga,Al)As layer functions as a “window” transparent for wide range of wavelength light. All the light falling on GaAs is absorbed by the N layer and non-equilibrium carriers – holes – are generated. This region must be produced very “cleanly” so it contains no recombination centers. These detectors have high sensitivity, fast response and high efficiency.

### 7.1.3 Materials for wave- and light-guides

Optic waveguides (light guides) are components for information transfer via optical signal. The source of optical signal is usually laser or laser diode. The light is modulated by an optical modulator and transmission system and it is then transported to the optical medium. The light is received by the photo-detector on the other end of the optic medium (fiber optic connection) and converted back to electrical signal.

The optic wavelength range offers immense possibilities of transmission capacity:

- symmetrical telephone cable (max. bandwidth / number of circuits): 552 kHz / 1920 circuits,
- coaxial cable: 60 MHz /  $1 \cdot 10^5$  circuits,
- waveguides: 100 GHz /  $5 \cdot 10^5$  circuits,
- optoelectronic connection: 500 THz /  $10^9$  circuits.

Optical medium between the transmitter and the receiver can be any material transparent for the used optic signal, e.g. atmosphere, vacuum or an optical waveguide. Modern optoelectronic systems utilize wavelengths from infrared ( $\approx 10^4$  nm) up to ultraviolet ( $\approx 10$  nm) part of the spectrum for information transport. Other options, how to expand this interval to the roentgen radiation ( $\approx 1$  nm) are being studied.

Most important light guide types are: **planar** and **fiber**.

**Planar lightguides** are utilized for short distance transfer of optical signal (usually in range of units of  $\mu\text{m}$  to mm). Used in miniature light guides, various optical connections, optic integrated circuits, two-dimensional lenses and others. **Passive light guides** consist of polycrystalline or amorphous thin layer. The integrated optic circuits are fabricated using appropriate lithographical technique. Light guides in combination with **active elements**, such as modulator (e.g.  $\text{LiNbO}_3$ ), lasers (YAG), and possibly other optic converters (opto-acoustic, magneto-acoustic...) are fabricated from single crystal medium.

**Principle** of planar light guide function: Dielectric layer of passive light guide is prepared on the substrate; the signal is transported in this layer. Surrounding environments has **refractive index**  $n_o$ , the substrate  $n_2$  and optical layer  $n_1$ . The following condition for optical layer  $n_1$  must be met:

$$n_o < n_1 > n_2.$$

#### **Material requirements:**

- total reflection:  $n_o < n_1 > n_2$ ,
- Selection of appropriate material for the substrate and layer – various glasses  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ , GaAs, ZnS,  $\text{LiNbO}_3$  and also some organic materials, e.g. polyester, hexamethyloxane...
- suitable layer preparation technology – deposition of vapor from vacuum or vacuum sputtering, thermal oxidation, ion bombardment, plasma polymerization ...
- high purity of the substrate, without any defects which could affect the active layer,
- maximal smoothness of the substrate surface
- high optical transparency of the transmission layer, attenuation less than 0.1 dB/mm.

#### **Fiber lightguides**

Main application is **long-distance information transfer**. Their attenuation of the signal is therefore the main attribute. The absorption of the transferred signal in the material is the most important signal-loss mechanism. This is caused mainly by Cr, Mn, Fe, Co, Ni, Cu and other compounds. Inhomogeneity, induced to the material during fiber production, can also cause some absorption. Another mechanism is harmonic oscillation of radical group  $\text{OH}^\cdot$  (water in the material). Other important attributes are: mechanical properties - mainly tensile strength, flexibility, resistance in its environment, lifetime, chemical stability, and small dependence of parameters on temperature and ionizing radiation. For the purpose of long distance electromagnetic wave transport, only the fiber optic light guides are of practical importance.

#### **Material requirements and basic fiber light guide types**

Fiber light guides are exclusively produced from glass. The active part of the fiber must be from pure high-quality or doped  $\text{SiO}_2$  with suitable fiber geometry. The simplest optic waveguide consist of optical fiber from homogeneous material surrounded by atmosphere.

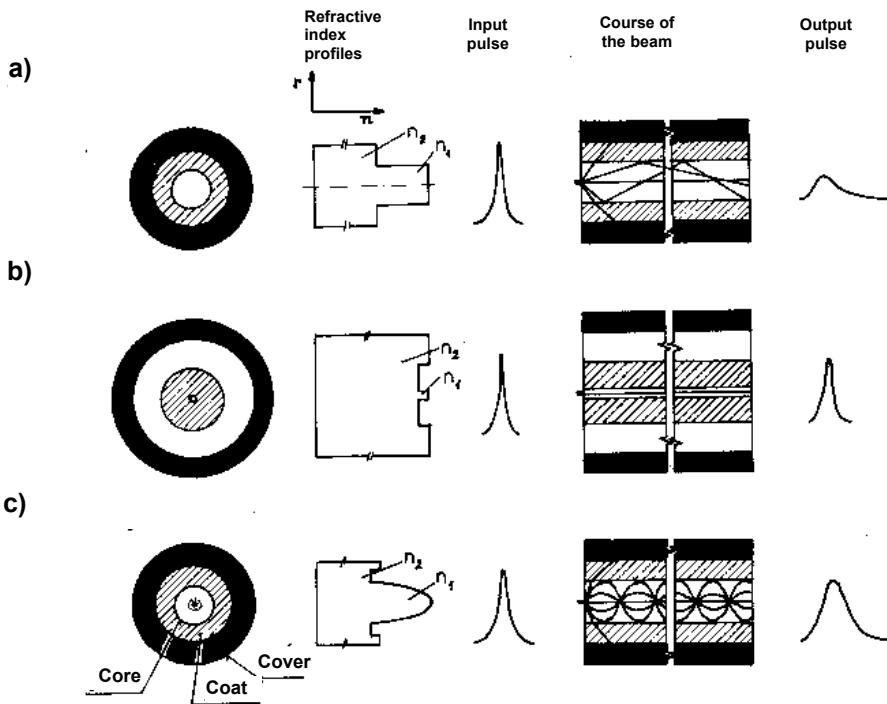
Basic material requirements for optic waveguides for transport of electromagnetic radiation:

1. The inequality:  $n_1 > n_2$  must be met,  
 $n_1$  is the refractory index of the fiber material,  $n_2$  is the refractory index of the environment surrounding the fiber.  
 The beam spreads through the waveguide and randomly reflects on the fiber-environment interface.
2. The beam incident angle on the core-cover interface must be smaller than critical angle for total internal reflection.
3. All the multiply-reflected beams (waves) must be in phase and not interfere with each other.

**Basic construction configuration of fiber** wave guides - Fig. 7.4.

Two different kinds of fiber waveguide are recognized: waveguides with step-index change of refractory index and waveguides with gradient-index change of refractory index. The refractory index depends on the frequency and this relationship is important for classification of the signal sources and corresponding spread of the signal in the waveguide

Waveguides with step-index change of refractory index consist of fibers with one or more layers of homogeneous material. Sometimes these also referred to as *layered (coated) waveguide*.



**Fig. 7.4** Three basic types of optical fiber: configuration geometry (core, coat, cover), relationship between  $n$  and the fiber diameter  $r$ , transport and distortion of the signal after passing through the waveguide

**Coated waveguide** has round core made of material with higher refractory index surrounded by coat made of material with lower refractory index. The refractory index profile is discontinuous on the core-coating interface. Fig. 7.4 lists examples of typical fiber waveguides and index profiles  $n$  of the waveguide with step and gradual profile in relationship to the fiber diameter  $r$ .

**Coated waveguides** are produced as single- or multi-mode (mode defines the relative position of electrical and magnetic field intensity vectors). Single mode waveguide have, even with very low refractory index, core diameter of about  $5 \mu\text{m}$  and outer diameter of the cover cca  $75 \mu\text{m}$  – Fig. 7.4a). Multi-mode waveguides have core diameter more than  $60 \mu\text{m}$  and outer cover diameter around  $75 \mu\text{m}$  – Fig. 7.4b).

Waveguides with gradient change of the refractory index, also known as **gradient waveguides** - Fig. 7.4c). **Gradient waveguides** are fabricated with various refractory index profiles. Commonly, the refractory index profile is parabolic relatively to the fiber diameter. The index is the highest in the fiber core; the index difference in the core and on the edge is 0.01 to 0.02. Production technology of these light guides is very complex. However they have very good transport properties.

**Materials for fiber waveguides**

Most frequently made of special high-purity glass, quartz, some kinds of plastic or combination of quartz and plastic. The glass is usually multi-component type, most frequently the sodium-calcium, boron-silicon, phosphate-silicate or alkali-lead glass. Plastic can either form the whole light guide or just protective coating on the light guide. Best results were achieved with PMMA (polymethylacrylate). Plastic coatings are usually made of polyvinyl fluoride or polymethyl siloxane.

ZnCl<sub>2</sub> is the best suiting material for transport of signal in over 2 μm range. Theoretical losses are 10<sup>-3</sup> dB/km. Other materials with low losses are halide glasses (Te<sub>2</sub>O<sub>3</sub>, AgCl and AgBr). Epoxy acrylates, polybutadiens and silicone are best suiting materials for primary light guide coating.

### Glass fiber light guide production technology

The production of this kind of light guide is very costly. The raw material for quartz optic waveguides is usually produced by CVD (Chemical Vapor Deposition). SiO<sub>2</sub> is deposited from its vapor, produced by decomposition of SiCl<sub>4</sub> in oxidation atmosphere. SiO<sub>2</sub> is deposited on quartz or ceramic substrate. The layers are porous, and are therefore sintered afterwards. The adjustment of the refractory index is facilitated by GeO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> (increase the refractory index) and other metal oxides or by addition of B<sub>2</sub>O<sub>3</sub> or fluorine which reduce the refractory index.

**Basic technology:** drawing from preform or dual crucible method.

#### a) Preform preparation

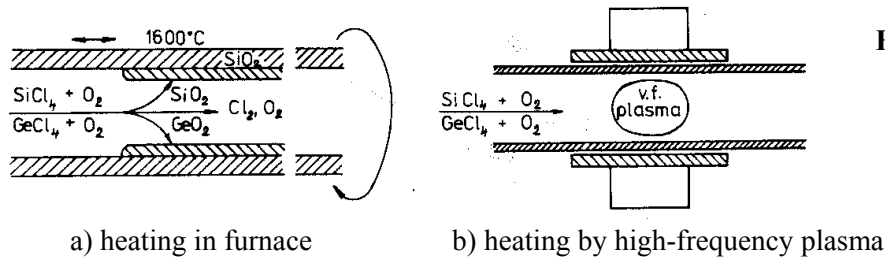


Fig. 7.5 Preparation of Si(Ge)O<sub>2</sub> layer by modified CVD method

- aa) method CVD – Fig. 7.5a). Appropriate substances are fed to the rotating quartz tube. Transport medium is oxygen. The reaction space is heated to the dissociation temperature of gaseous SiCl<sub>4</sub> and GeCl<sub>4</sub>. Desired Si and Ge oxides condense on the inner wall of the tube in desired ratio. During the decomposition process, the high-temperature zone is shifting along the tube to produce homogeneous and uniform layer of Si(Ge)O<sub>2</sub> along the whole tube. The new layer of Si(Ge)O<sub>2</sub> has higher refractory index than the former SiO<sub>2</sub> tube. Precise dosing, the uniformity of the heating, rotation and shift of the zone all correspond to the final properties of the layer.
- bb) high-frequency plasma application – Fig. 7.5b). This process takes place at pressures up to 2.5 kPa and lower temperature – up to 1000 °C.
- cc) preform preparation – after the condensation phase, perfectly round rod – **preform** – is slid inside the tube at elevated temperature - Fig. 7.6.

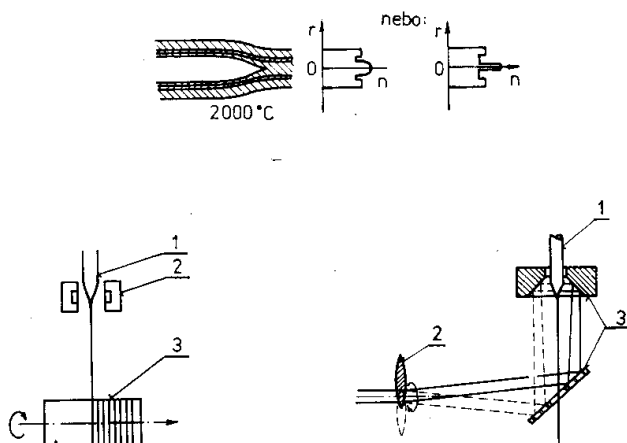


Fig. 7.6 Optic fiber production

a) Preform preparation (typical dimensions: diameter of 5 to 15 mm, 300 to 1500 mm length).

b) Process of drawing the fiber from preform.

On the left – normal heating to temperature 1900 °C.

- 1 – preform,
- 2 – heater (maximum uniformity of heating),
- 3 – fiber reel

On the right – laser heating.

- 1 – preform.
- 2 – eccentric rotating lens,
- 3 – mirror system.

Radial speed is 0.3 to 2 m/s.

#### b) Optic fiber preparation

Fig. 7.6 schematically depicts the drawing process of optic fiber waveguide. The fiber diameter is 50÷100 μm. The preform is locally fused and a wire is drawn on rotating reel which produces necessary traction. The fiber geometry and reeling parameters are adjusted by control signal. The right side of Fig. 7.6 shows the cleanest and best controllable laser heating. Laser beam passes through a rotating lens and is reflected by a mirror; this produces

circular movement and from there, the beam is reflected on the quartz rod and fuses the end of the preform. The fiber passes through the center of concave mirror and put on a reel.

**Rod in tube method** - a rod (future core of the light guide), made of material with desired refractory index, is placed in a tube (future coating of the light guide) with desired coating refractory index. Prepared semi-finished product is heated on one end to the temperature of glass fusion and a fiber is then drawn from this spot. This method is eligible for production of cheaper multi-mode waveguides.

**Double crucible method** – inner crucible contains melt core material and the outer crucible contains melt coating material. The advantages are possibility of infinite-length waveguides (while refilling the crucibles), large diameter adjustments of core and coating diameter and especially production of superior and well-defined core-coating interface. The outflow velocity can go as high as several m/s. Minimal attenuation of thusly produced waveguide is 5 dB/km. In case of the mouth of the inner crucible being higher than the mouth of the outer crucible, the melt materials mix by diffusion or ionic exchange during drawing of the fiber. Fiber with desired refractory index is thus produced.

## 7.2 MATERIALS FOR MEMORY MODULES

The memory technology strongly contributes to the performance of modern digital computers. Important factors are memory capacity, their speed and price.

### Electronic information storage memory

Basic classification of semiconductor memories:

By the basic technology:

**bipolar memory** and **MOS memory.**

By operation regime:

**static** and **dynamic memory.**

By the means of data reading and recording: **rewritable** and **permanent.**

**Bipolar semiconductor memory** is utilized as static memory. Flip-flops are the basic type. They are characterized by their high speed and lower bit density of the chip.

**MOS memory (Metal–Oxide–Semiconductor)** has higher bit density, is cheaper but also slower than bipolar memory.

**Rewritable memory** is usually bipolar or MOS type, static and dynamic. Allow for arbitrary reading and writing of data.

**Permanent memory** is bipolar or MOS type, static memories are known under the abbreviation of ROM (Read Only Memory) and can be divided in several groups:

- PROM** – programmable ROM ,
- EPROM** – erasable programmable ROM memory, can be erased using UV light,
- REPROM** –reprogrammable ROM memory,
- EEROM** – electrically erasable ROM memory,
- CCD memory (Charge Coupled Device).**

**Principle:** The charge carriers accumulate in potential well under control electrodes held at certain voltage; change in voltage of these electrodes results in transport of carriers from on electrode to the other. Distance between electrodes is 3 to 5  $\mu\text{m}$ .

**Technology of production** – see Power Point presentation – **MG CMOS**

### Memory for magnetic information storage

Typical memories of this type store the information on a ferromagnetic cores (cylindrical, toroid cores or transfluxors) and are nowadays being replaced by **bubble memory**. These bubbles comprise of **cylindrical magnetic domains**, separated from its surroundings by **cylindrical domain wall**. This wall changes the angle of magnetization vector by  $180^\circ$ . Magnetic bubble present at certain spot means that the information value is e.g. „1“. The active magnetic layer of the bubble memory must have single axis anisotropy. Most common material is **magnetic garnet**. Generation and transport of magnetic bubble (max. speed is 5 to 20 m/s, bubble diameter of units of  $\mu\text{m}$ ) is provided via so called „superstructure“. This superstructure usually comprises of thin layer from permalloy deposited on magnetic garnet layer. The bubble transport is facilitated by e.g. non-homogeneous magnetic field.

## 7.3 MATERIALS FOR PHOTOVOLTAIC (SOLAR) CELLS

### **Principle of light to electricity conversion**

Solar cell consists of two layers of crystalline silicon. The upper layer is usually phosphorus (N-type semiconductor) doped and the lower layer is imprinted by silver grid (Ag) with aluminum (Al) addition. The aluminum penetrates the silicon substrate during the production process thus forming P layer. NP junction is formed between the layers which prevent transport of free – superfluous electrons from N layer to the P layer – so called junction barrier. Light falling on the upper N-type conveys its energy to the atoms of the crystal lattice and electrons are thus released; these electrons cannot cross the NP junction barrier to enter the P layer and are accumulating in the layer with the N-type conductivity. Accumulation of free electrons in the upper layer creates electric potential of about 0.6 V per one solar cell. When connected to the electric circuit, the superfluous electron start flowing through the upper layer conductor to the lower, electron-deficient, layer. The basic attribute of the NP junction is that transient of electrons from P to N layer is easier than the opposite. Therefore the P layer free electrons replace the released electrons from N layer thus closing the circuit. The sunlight works as an energy source.

### **Materials for solar cells:**

**Silicon** – typical precursor for modern solar cells production:

Polycrystalline or amorphous silicon – suitable for lower power outputs, main advantage is good efficiency, even in low-light conditions.

Single-crystal silicon – suitable for higher power outputs, higher power output than polycrystalline cells in low-light conditions. Single crystal cell of about 100 cm<sup>2</sup> area can generate 3 to 4 amperes.

**Gallium arsenide (GaAs)** – main advantages are higher efficiency – 20 %, higher space radiation resistance and allowable operation temperatures higher than 100 °C.

### **Utilization of solar energy**

Solar energy can be used for heat production (domestic hot water production, water pool heating, house heating, recreational facility, greenhouses, drying room).

### **Active solar systems**

The solar energy is converted to heat by so called **solar collectors**. Heat produced in collectors is used directly for heating, reheating, hot water production or it can be stored in accumulation reservoirs and used later (at night, lower light days). Active systems collect heat in liquid or vacuum (flat and tubular) collectors.

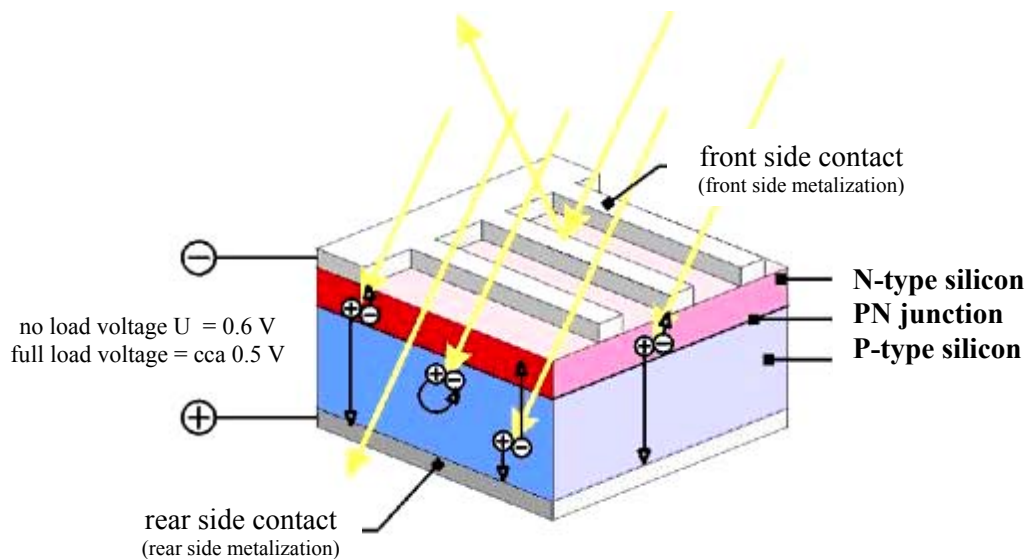
### **Utilization of solar energy for electricity production**

Electricity is produced utilizing the photovoltaic cells. This energy is either transferred to the distribution network or used for, e.g. summer houses, coffee shops, parking automats, night lighting, operation of small home appliances. Produced energy can be consumed immediately or stored in accumulators and used later (low-light periods). The building block of a photovoltaic module is a single solar cell. They are connected together either in series or in parallel, depending on desired electric parameters.

### **Principle of photovoltaic cell**

Basic part of the photovoltaic cell is the PN junction; it utilizes the photovoltaic effect – matter absorbs the photons of falling sunlight and release electrons. Free electric charges, electrons and holes, are thus generated in the semiconductor; these are, already as electricity, transferred (via charge controller) to an accumulator or appliance – Fig. 7.7.

The efficiency of solar cells is improving constantly. Efficiency of mass produced amorphous Si is only 8 to 9 %, lab-prepared multilayer cells from amorphous SiC/amorphous Si have efficiency of 13.4 %, amorphous Si/amorphous Si-Ge multilayer cells 14.3%, amorphous Si/polycrystalline Si double – terminally layered cells 15 % and quadruple terminally layered amorphous Si/polycrystalline Si have efficiency of up to 21 %.



**Fig. 7.7** Construction configuration of the photovoltaic cell

## 7.4 LIQUID CRYSTALS

Some organic compounds can be found in more than just liquid and solid state. These compounds are called liquid crystals and their molecules are often called **mesogens**. Different phases between solid and liquid state are liquid crystal phases or also meso-phases. Molecules of these matters are usually long and narrow. **Liquid crystal phase** has some attributes of both liquid and solid phase. It is fluid as a liquid but also has optic and electromagnetic properties like a solid. Oriented configuration of the molecules corresponds to many interesting phenomena occurring in the material. Passing light can be polarized, depending on the position of the molecules in the material. Another important property is their behavior in electric field. Molecules are neutral. Nevertheless, the electrical charge in different parts of the molecule can differ substantially. Molecule with one part positive and other part negative becomes a dipole. In electric field, this dipole tends to turn in the field direction.

### Types of liquid crystal types

Heating of common solid above their melting point produces isotropic liquid. However in some organic compounds, one or more liquid crystal phases (meso-phases) with differing structure occur. In all cases, these are matters with anisotropic molecule shape (resembling rods, plates, discs etc.).

Liquid crystal phases occur either above melting point of some organic compounds (**thermo-tropic**) or in solution with suitable solvent, typically water (**lyo-tropic phase**).

Based on the molecule configuration, the liquid crystal phases can be divided into several groups:

#### A. Nematic phase

Molecules are independent and can move freely in all directions. However elongated molecules are oriented in certain direction called the director,  $n$ . It is so called orientation configuration, typical for liquid crystals. Molecules rotate freely along both their shorter and longer axis. Molecules in nematic phase flow in all three directions and their viscosity is close to that of isotropic liquid phase.

#### B. Chiral nematic – cholesteric phase

Molecules tend to be turned slightly relative to each other. Their direction is slightly different in every layer and together they form a „spiral”. In display industry, this is the most utilized type of liquid crystal material. These displays, employed for example in wristwatches, are called Twisted Nematic LCD. The nematic liquid crystal in these displays is set between transverse polarization filters. Their inner surface is specially prepared so the molecules on their surface are aligned with the polarization filters. If there are no molecules between the polarization LC filters, light cannot pass through. However the rotating molecule structure transmits light and



allows it to pass through the second polarization filter. Voltage causes the spiral to decompose and most of the molecules align in the direction of the electric field. Result is the same – the light cannot pass.

### C. Smectic phase

There is a single-dimension arrangement of the molecules, as in layered structure. The layers can slide on each other and flow in one plane. Some smectic phases have multi-dimensions arrangement. The molecules rotate in the layers so their axis is still in the plane defined by the layer.

### D. Columnar phase

The molecules in columnar – discotic phases in shape of discs or plates organize into relatively firm columns together forming cubic or hexagonal structure. Bond between individual columns is weak, so the columns can glide freely. Ferroelectric liquid crystals are promising variant of an LCD. Their main difference compared to nonmagnetic structures is their own, adjustable, polarity. The polarity of single cell or the polarity of whole crystal can be changed almost permanently by external force. In practice, this means that image on reflex ferroelectric TFT (thin-film transistor) LCD display will be visible even during power shortage. Their major advantage is their speed and wide viewing angles.

### Liquid crystal materials

These are polyanilin based compounds exhibiting solid phase properties in one dimension and liquid phase properties in other. Some parts of biomass provide raw material for liquid crystal production. Those are saccharides, more precisely saccharide surfactants.

### Liquid crystal application

**Electro-optic displays** in wristwatches, calculators and many other devices. Utilize the change of optical properties by electric field.

**Screens for personal computers – LCD screens.** Gray scale must be provided for this purpose, it is later transformed to color scale by various color filters.

Cholesteric liquid crystals found its application as **temperature indicators** and temperature mapping (revealing inflammation or tumor bearings).

### Principle of LCD screen

Backlight is necessary for the image of the screen to be readable – this is usually facilitated by electroluminescence gas-discharge lamp. Only a portion of the light passes through the polarizer resp. only horizontal or vertical polarized light. There is a liquid crystal layer between two orientation filters. Liquid crystal molecules in idle state are dis-aligned, the mis-orientation is limited by orientation filter. The light from the backlight source passes through the molecules in idle state – Fig. 7.8 a) – the display “glows”. Light passing through the polarizer becomes horizontally polarized. This light further passes through the liquid crystals. The mis-orientation of the liquid crystal molecules causes the passing light to be turned thus becoming vertically polarized. Vertically polarized light passes through the polarizer and the display therefore “glows”. If we connect the liquid crystal to the alternating power source, its inner structure changes. Molecules of the crystal are no longer mis-oriented but aligned. The light passing through a layer of liquid crystal therefore cannot change its polarization from horizontal to vertical and is stopped by polarizer which lets through only the vertically polarized light. The screen remains dark (the backlight does not go through) – Fig. 7.8 b). It is obvious that the orientation of molecules controls whether the light passes through or not. In practice, the limit states (light passes, does not pass) are not sufficient, amount of light, resp. the brightness, needs to be regulated. This can be achieved by adjustment of voltage supplied to the electrodes. Every spot on the screen contains red, green and blue filter, placed on the upper glass plate. The color screens always have a backlight. Passing the light to the color filters and mixing it produces the final color.



Fig. 7.8 a) Idle state – the light is allowed to pass

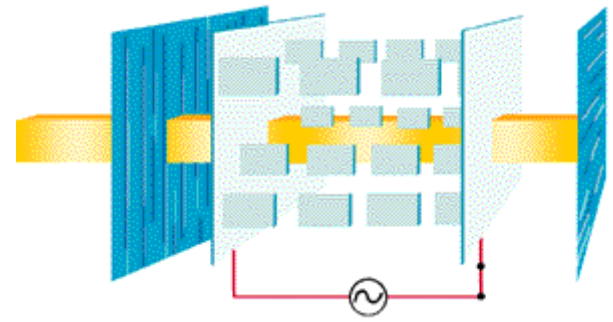
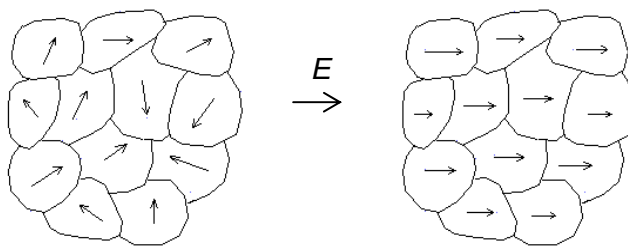


Fig. 7.8 b) Voltage applied - light cannot pass

## 7.5 FERROELECTRIC MATERIALS

**Ferroelectric materials (ferroelectrics)** consist of polar molecules. Susceptibility of these matters (e.g. Seignett salt, potassium phosphate and barium titanate) is controlled, up to certain temperature, by electric field intensity  $E$  which also exhibits as **electric hysteresis**. Cyclic change of  $E$  produces hysteresis loop similar to those of ferromagnetic materials.

**Ferroelectrics** are a special group of dielectrics, characterized by **occurrence of spontaneous polarization**. Matters with spontaneous polarization typically have **domain structure** – see Fig. 7.9 and Fig. 13. **Domains** are macroscopic structures of the insulator, in which, the charged particles are spontaneously completely polarized, and exhibit **dipole moment without any external electric field**. Number, shape and orientation of domain correspond to the tendency of the system to reach minimal-energy state. Total electric moment vector of every spontaneously polarized domain has certain direction; the domain directions are not aligned. The electric moment vector product of all spontaneously polarized domains is zero, the matter appears to be non-polarized. The electric moments of singular domains quickly align in **external electric field** (elastic shift of ions in domains) in the direction of el. field and the polarization is substantially increased.



a) without electric filed    b) inside electric field

Fig. 7.9 Structure of ferroelectrics

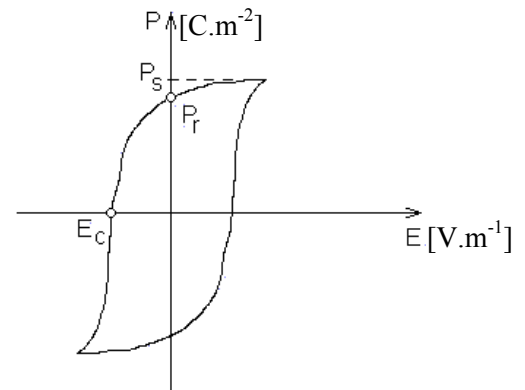


Fig. 7.10 Hysteresis loop of ferroelectric matter

Spontaneous polarization depends on temperature, frequency and intensity of the external electric field. The biggest peculiarity of the ferroelectrics is non-linear dependency of the polarization  $P$  on electric field intensity  $E$  and existence of electric hysteresis. Characteristic **hysteresis loop** is shown on Fig. 7.10. It is obvious that at certain gradient of electric field the material becomes saturated, with all domains oriented in the direction of the field; further increases of the field intensity has no effect on polarization. The loop is characteristic by saturated polarization  $P_s$ , remanent polarization  $P_r$ , which is polarization remaining in material after lowering the electric field intensity to zero and by coercive intensity of electric field  $E_c$ , corresponding to the field intensity necessary for complete depolarization of the ferroelectric ( $P = 0$ ). Ferroelectrics remain spontaneously polarized up to certain temperature, Curie temperature  $T_c$ . The Brown motion energy of ions above  $T_c$  is so high that it interferes with aligned ions in neighboring cells and ferroelectric properties of the material disappear.

**Barium titanate ( $\text{BaTiO}_3$ )** has, above  $120^\circ\text{C}$ , ideal cubic structure of perovskite type – Fig. 7.11. In the center of the cube, with barium cations in the corners, there is a titanium cation surrounded by six oxygen anions which are placed in the center of the cube faces. Bellow  $120^\circ\text{C}$ , the elementary cell elongates in direction of one edge and the structure is changed to tetragonal – ditetragonal pyramidal type. Spontaneous polarization also occurs; its

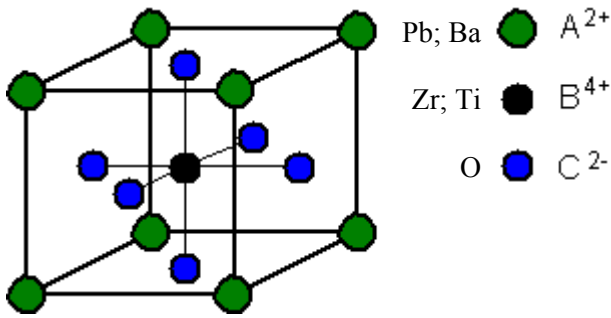


Fig. 7.11 Basic cell of perovskite structure ABO<sub>3</sub>

A<sup>2+</sup> direction corresponds to the direction of the dilatation. Radiographic study revealed that the cation is not exactly in the center of the cell, it is slightly shifted in the direction of spontaneous polarization. Oxygen anion which it was shifted towards to, shifts in the opposite direction, closer to the titanium cation. This opposite-direction shifts of Ti<sup>4+</sup> and O<sup>2-</sup> explains the spontaneous polarization.

Important attribute of ferroelectrics is the permittivity  $\epsilon_r$ ; it is considerably higher than permittivity of common dielectrics. Thermal dependence of relative permittivity  $\epsilon_r$  in various ferroelectrics exhibits very sharp maximum at temperature  $T_c$  (e.g. for BaTiO<sub>3</sub> at  $T_c = 393$  K) – Fig. 7.12.

Other (lower) maximums can be occur bellow Currie temperature. At present, the ferroelectrics based on BaTiO<sub>3</sub> are mostly utilized. By other elements addition, we can adjust the properties of the ferroelectric. For example, these can lower the  $T_c$  towards lower temperatures or reduce the maximum permittivity – they flatten the sharp maximum on the  $\epsilon_r = f(T)$  curve, however don't change the position of Currie point.

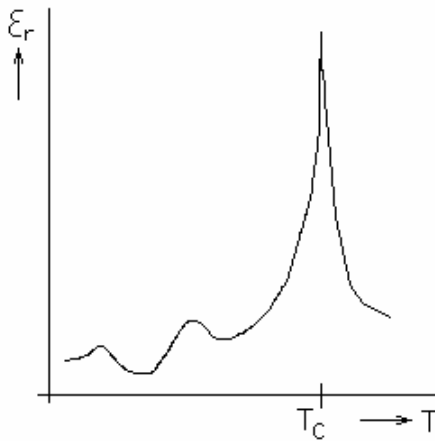


Fig. 7.12 Thermal dependency of permittivity of BaTiO<sub>3</sub>

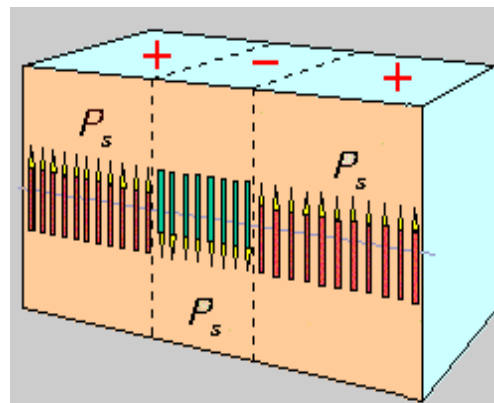


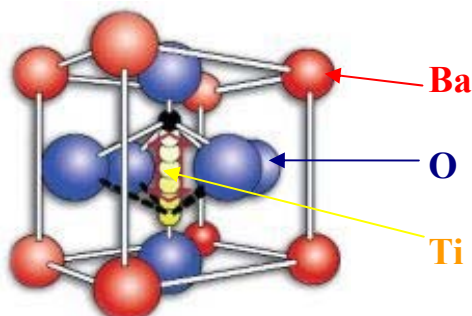
Fig. 7.13 Ferroelectric domain

Substantial flattening can lead to reduction of the maximum permittivity to 1000 - 2000; the permittivity is only mildly affected by temperature (mild maximum). Application: **miniature high-capacity condensers**. Big advantage is that BaTiO<sub>3</sub> ferroelectrics can be produced by powder metallurgy. Their greatest asset is simple, undemanding miniaturization of the circuits. It utilizes high permittivity ( $\epsilon_r = 150 \div 15000$ ) for example of miniature ceramic condenser production. Practical application also utilize the **piezoelectric properties** of ferroelectric, e.g. in **resonators** and in **electromagnetic converters** (gramophone pickups).

Ferroelectric also exhibit some other interesting properties, such as **pyro-electric** (temperature dependent polarization change) or **opto-electric properties**.

### Applications of ferroelectric crystals

Example of application of ferroelectric materials is memory medium called **FRAM**. The basic part of FRAM memory is **ferroelectric crystal** which allows the memory to operate as RAM but also to permanently store data.



Crystal subjected to an electric field shifts its central atom in the direction of the field (Fig. 7.14) and passing current creates power surge. Internal circuits recognize this surge and switch on the memory. Central atom remains in this position even after the electric field has been removed and the state of the memory preserved. **FRAM keeps the stored data even after the source has been removed**, it is fast and does not wear out.

Fig. 7.14 Ferroelectric crystal BaTiO<sub>3</sub>

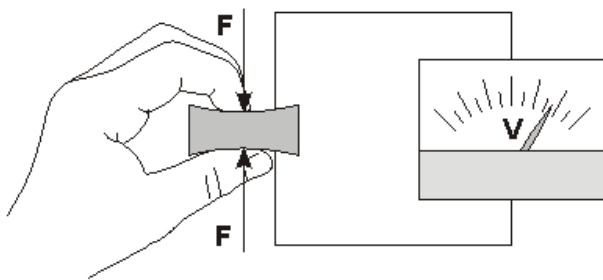
**Application of FRAM:** data storage and backup, configuration storage, permanent data buffer, electricity, gas, and water consumption measurement, automobiles (air-bags), laser printers and copiers, industrial control machinery, cable network control, set top boxes and home appliances, industrial and bank systems ... Future applications involve hard disc with quick data buffer.

Another application of ferroelectrics: satellite and land communication, microwave applications with higher operation frequencies than the operation frequency range of silicon. Electro-optic devices: shutters, optic components with controllable birefringence.

## 7.5.1 PIEZO-ELECTRICS

### PRINCIPLE OF PIEZOELECTRIC EFFECT

**Mechanical pressing** of piezoelectric crystal by force  $F$  **deforms the lattice** – this results in **electric voltage generation** (Fig. 7.15) on deformed facets of the crystal. Piezoelectric effect occurs only on **asymmetrical crystals** – e.g. barium-titanium ceramics and quartz. Magnitude and polarity of the voltage correspond to the magnitude and direction of crystal deformation. Voltage applied on the piezo-crystal results in deformation of the crystal; alternating voltage manifest as mechanical oscillation of the crystal.



Piezoelectric components are produced by cutting a plate from quartz crystal with its edges parallel to axis of the crystal ( $x$  – electrical axis,  $y$  – mechanical axis,  $z$  – optical axis). Force applied **perpendicularly to the optical axis**, electrifies the crystal and a voltage is generated on planes perpendicular to the electrical axis.

Fig. 7.15 Piezoelectric effect

### PIEZOELECTRIC MATERIALS

#### Basic classification:

- Crystalline piezoelectric materials (single crystals).
- Polycrystalline piezoelectric materials (piezoelectric ceramics).
- Organic polymers (piezoelectric polymers).

#### a) SINGLE CRYSTAL PIEZOELECTRIC MATERIALS

Typical representative of this group is **quartz ( $\text{SiO}_2$ )**, crystallizing in trigonal crystal system. Desired properties and attribute correspond to the cut orientation. Other affected parameters are their geometrical dimensions, ratio between them, sizes and position of electrodes and their shape.

#### Material examples:

- lithium niobate  $\text{LiNbO}_3$ ,
- lithium tantalate  $\text{LiTaO}_3$ ,
- germanium-bismuth-oxide  $\text{Bi}_{12}\text{GeO}_{20}$ ,
- triglycine sulfate TGS.

#### Semiconductive materials:

- beryllium oxide  $\text{BeO}$ ,
- cadmium sulfate  $\text{CdS}$
- gallium arsenide  $\text{GaAs}$ ,
- gallium phosphide  $\text{GaP}$ ,
- zinc oxide  $\text{ZnO}$ ,
- zinc sulfide  $\text{ZnS}$ .

#### b) POLYCRYSTALLINE CERAMIC MATERIALS (PIEZOELECTRIC CERAMICS)

#### Material examples:

- barium titanate  $\text{BaTiO}_3$
- lead zirconate  $\text{PbZrO}_3$
- lead titanate  $\text{PbTiO}_3$

- lead zirconate titanate PZT (**solid solution of  $\text{PbZrO}_3$  and  $\text{PbTiO}_3$** ).

### c) ORGANIC POLYMERS (PIEZOELECTRIC POLYMERS), also called polar polymers:

#### Material examples:

- polyvinyl chloride PVC,
- polyvinyl fluoride PVF,
- difluor polyethylene PVF<sub>2</sub>.

## PRODUCTION OF PIEZOELECTRIC MATERIALS

For practical use, specifically shaped cuts are prepared from the piezoelectric material. These are most commonly rod or plate shaped cuts. Rods are typically rectangular. Plates are either rectangular and also round shaped.

## APPLICATION OF PIEZOELECTRIC MATERIALS

Piezoelectric materials are actively applied in aviation, cosmonautics, military, industry, hospitals and at home.

**Beaudoin manometer** – study of periodic changes.

**Beaudoin accelerograph** – acceleration measurements: earth, roadway bridges and reinforced concrete structure vibrations measurements in transport or construction engineering.

**Ultrasound defectoscopy** – detection of hidden material defects or in **medicine** (ultrasound imaging of human fetus, ultrasound micro-massages, removal of kidney or gallbladder stones). Piezoelectric high voltage power source is also **gas igniter**: pressed button strongly deforms the crystal generating voltage high enough for a spark to jump between the electrodes.

### Application PZT ceramics

Piezoelectric ceramics PZT ( $\text{PbZrO}_3$ ) is widely utilized electric material for application in **sensors, ultrasound generators, actuators and convertors**.

Main devices utilizing PZT ceramic materials are:

- resonators – ultrasound cleaning and welding, ultrasound sources for medical diagnostic devices, liquid spraying, drug inhalers,
- convertors – measurement of non-electric attributes such as force, acceleration, pressure,
- lighters, piezoelectric transformers,
- crystal filters,
- actuators – piezoelectric, ultrasound motors, fine shifters in optics and in scanning microscopy,
- oscillation and noise dampening,
- impact sensors for an airbag deployment, parking sensors, ultrasound control of toys.

**Piezoelectric pressure sensors** – dynamic pressure, compressive forces, acceleration, deviation and mechanical stress measurements.

**Piezoelectric accelerometers** – measurement of vibrations in range of 0.1 Hz to 10 kHz at temperatures up to 240 °C. Main attributes: low dependency (high stability) of the sensor's sensitivity on temperature, frequency and time, interference resistance. Application: monitoring of machinery, transmission, motors and roller bearings.

**Piezoelectric oscillation sensors** – simple construction, reliability, high sensitivity.

**Piezoelectric materials in printers** – ink shooting utilizes piezoelectric oscillation of crystalline membrane.

**Application in automotive industry** – common-rail direct fuel injection in diesel engines.

**Application of piezoelectric cuts in ultra-acoustics** – ultrasonic material testing, water level measurements in inaccessible areas, securing waterways, liquid and gasses velocity measurements.

**Piezoelectric microphones, gramophone convertors and speakers**

**Ultrasound generator, sound signaling**

**Acoustic emission pickups**

**Piezo-ceramic acoustic converter**

**Piezoelectric converter**

**Piezoelectric ringer**

**Piezoelectric gas igniter**

# 8. INSULATORS

## 8.1 ATTRIBUTES OF INSULATORS AND DIELECTRICS

**Insulators** are materials with no free electrons or other free charge carriers (e.g. ions), and therefore are not electrically conductive. Electric insulators are utilized predominantly for conductor (cable) **insulation**, separation of conductive parts of appliances, and to enhance capacity of capacitors. Particles with electric charge are bound to certain places in the insulator lattice, and cannot be, under normal circumstances, moved away from this position by electric field. This is why there can be an electric field present in an insulator.

**Permittivity** describes the effect of electric field on electric conditions in the insulator. It is defined by **electric induction  $D$**  in insulator divided by **electric field intensity  $E$** , in which it is placed:  $\epsilon = D / E$ . **Relative permittivity  $\epsilon_r$**  is dimensionless attribute with value (for an insulator) in range of 1 to  $10^4$ . The value for air is 1, for some insulators up to 500.

**Permittivity of an insulator** is  $\epsilon = \epsilon_0 \epsilon_r$ , where **permittivity of vacuum  $\epsilon_0 = 8,859 \cdot 10^{-12} \text{ F} \cdot \text{m}^{-1}$** .

**Dielectric** is an insulator with ability to be polarized. Therefore all dielectrics are insulators but no every insulator is dielectric.

## 8.2 POLARIZATION OF DIELECTRICS AND THEIR PROPERTIES

Placing the insulator in electric field results in phenomenon called **polarization of dielectric**. Polarization causes atoms and molecules of the dielectric (**non-polar** dielectric) to become dipoles by attractive and repulsive forces of electric field – the particles with electric charge in atoms and molecules become **non-symmetrically** distributed (electrons closer to one side, atom cores closer to the opposite side). This is called **atomic polarization**. Some materials (**polar** dielectrics such as water) contain electrical dipoles even without external electric field. Their orientation is random and polarization causes the dipoles to align in one direction. This polarization is called **orientated polarization**. Electric field causes the charge carriers to move and to align in the direction of el. field. Degree of polarization of dielectric - **permittivity**.

**Polarization of dielectrics** depends on structure and on the intensity of external electric field; it is evaluated based on electric induction  $D$ . After the electric field has been removed, the particles return to their original position. The particles move until equilibrium is reached – so called **displacement current**. During this process, energy is dissipated. All electric dipoles have, during polarization, same polarity – opposite to the polarity of external el. field.

### **Types of electric polarization:**

- 1) deformation - electronic  
(elastic) - ionic
- 2) relaxation - dipole  
- ionic relaxation
- 3) volume - interlayer  
(migration) - high-voltage
- 4) special - spontaneous  
- resonance

### **Deformation (elastic) polarization**

Very fast, loss-less short-distance displacement of elastic-bonded charges (electrons, ions). Deformation polarization in dielectric is loss-less and practically independent on neither temperature or frequency.

#### **Electron polarization**

Electron polarization exhibits itself in all insulators by displacement of atoms and electrons in atom shell. Settling time  $\tau = 10^{-15}$  to  $10^{-13}$  s. Electron polarization is temperature independent,  $\epsilon_r$  decreases with temperature.

#### **Ionic polarization**

Ionic polarization, occurring mainly in insulators with metal or ionic bonds, causes displacement of ions with positive or negative charge. Ionic materials (electrostatic forces) have the settling time  $\tau = 10^{-13}$  to  $10^{-12}$  s.

Frequency independent, but thermally dependent. Increase in temperature results in increase of inter-atomic distances → polarization increases.

### Relaxation polarization

Occurs mainly in insulators with charged particles, e.g. dipole molecule or ions, gradually become polarized by the electric field. Relaxation polarization is temperature dependent and energy is dissipated in dielectric.

#### Dipole relaxation polarization

Occurs in polar gases and liquids consisting of dipole molecules. Dipole orientation in the  $E$  direction is disturbed by thermal motion.

#### Ionic relaxation polarization

Occurs in dielectrics with irregularly configured ions, e.g. amorphous structures: inorganic glasses and glass phase ceramics. Polarization of ions in the structure gaps. Exponential time dependency (both the initiation and abatement). Thermally dependent – the number of polarized ions increases).

### Volume polarization

Free charges motion (migration polarization). Occurs in materials with inhomogeneous structure – carriers accumulate on the interface → volume charge.

#### Interlayer polarization

Occurs in mica and insulators with layer-like structure (cardboard, impregnated paper, relanex, ...).

#### High-voltage polarization

Occurs in insulators with uni-polar conductivity (ions in inorganic glasses) in strong DC voltage. The strong voltage causes release of carriers and their movement towards the electrode; layer near the other electrode is deprived of the carriers → unequal charge distribution.

### Special polarization

#### Spontaneous polarization

Occurs in dielectrics with non-organized domain structure (ferroelectrics). The voltage  $\bar{E}$  → domain alignment, spontaneous polarization is thermal dependent: Curie temperature  $T_c$ .

Dependency on  $\bar{E}$ : non-linear, dielectric hysteresis, saturation.

#### Resonance polarization

At very high frequencies (visible spectrum). Frequency comparable to the particle oscillation.

### Dielectrics divided by the polarization type

- non-polar (neutral) insulators: materials with covalent bonds without dipole moment, only electron polarization,
- polar insulators: covalent bonds with dipole moment, electron and dipole polarization,
- ionic crystals: electron and ionic polarization,
- amorphous ionic insulators: electron, ionic and relaxation polarization,
- ferroelectrics: electron, ionic and spontaneous polarization.

### Permittivity of gasses

Gas properties: low density → low permittivity (very weak polarization),  $\epsilon_r \cong 1$ .

### Permittivity of liquids

Insulators – only liquids with covalent bond.

Neutral - only electron polarization,  $\epsilon_r \sim 2$  to 2.5.

Polar - electron + dipole polarization  $\epsilon_r \sim 3$  to 6.5.

$\epsilon_r$  depends on temperature and frequency.

Permittivity of solid insulators depends on the type of polarization:

Non-polar – only electric polarization,  $\epsilon_r \approx 1.8$  to 2.5. Frequency independent, slightly dependent on temperature (see liquids).

Ionic - electron + ionic polarization, various  $\epsilon_r$ ,

Polar insulators - electron + dipole relaxation polarization (same as polar liquids).

Ferroelectrics – same as ionic materials + spontaneous polarization → high  $\epsilon_r$ , thermal dependency – Curie point  $T_c$ .

Under  $T_c$   $\epsilon_r \approx 1000$  ÷ 10000, dielectric hysteresis. Materials: **BaTiO<sub>3</sub>**, ceramics.

**Dielectric losses** represent

- losses in dielectric caused by the electrical field,
- losses caused by carrier motion (both free and bonded),
- inhomogeneity of dielectric,
- partial discharges.
- Direct field – mostly conductivity losses
- Alternating field – much higher losses:  
Conductive ... all insulator types,  
Polarization ... idle types of polarization,  
Ionization ... gasses and gas cavities.

Expression of losses:

|                              |                             |
|------------------------------|-----------------------------|
| - loss factor                | $\text{tg } \delta$ ,       |
| - loss power output          | $P_z$ [W],                  |
| - specific dielectric losses | $p_z$ [W·m <sup>-3</sup> ]. |

### **Main types of dielectric losses:**

Conductive: Occurs in all insulators (free charge carriers) Joule losses, transmission of kinetic energy from carriers to bonded atoms → heat generation.  $P_z$  does not depend on  $f$ ;  $\text{tg } \delta$  decreases. Thermal dependency increases exponentially with conductivity.

Losses correspond to the total area of hysteresis loop, affecting the thermal motion of particles.

For relaxation polarization – maximum  $\text{tg } \delta$ , temperature and frequency dependent.

Layered insulation – interlayer polarization losses.

For ferroelectrics – thermal dependency ( $T_c$ ).

Resonation losses – outside the range of technical frequencies (IR spectrum).

Ionization: in gasses above critical el. field level, also in cavities of solid insulators.

### **Electrical conductivity of insulators**

#### **Electrical conductivity of gasses**

Gasses are, at normal conditions, good insulators.

Above critical level of el. field – impact ionization – self-contained conductivity.

Non-independent conductivity – by external ionization:

#### **Impact ionization**

#### **Photo-ionization**

#### **Thermal ionization**

Surface emission – release of electrons from electrode surface, energy is either heat or radiation falling on the cathode surface.

Simultaneously with ionization, **recombination** takes place – ions charge is neutralized..

#### **Electric conductivity of liquid insulators**

Covalent bond, sufficiently strong, high mobility of particles in liquids.

Polar insulators

- dissociation of their own molecules → greater conductivity,
- impurities dissolution → greater conductivity.

El. conductivity thermal dependency is described by Arrhenius equation:

$$\gamma = A \exp^{-Q/RT} \quad A, Q \text{ and ... constants}$$

Electric conductivity of liquids corresponds to viscosity  $\eta$

Electro-phoretic conductivity – charge carriers are colloid particles, their motion in electric field is the same as during electrolysis, however without chemical changes on electrodes – occurs mostly in mineral oils.

#### **Electrical conductivity of solid insulators**

Conductivity is caused by:

- ions of insulator,
- ions of impurities (admixture),
- electrons (in strong electric fields).

Non-polar materials

- their molecules do not dissociate, high  $\rho = 10^{14} \Omega \cdot \text{m}$  (paraffin wax, polyethylene, ...).

Ionic crystals

- free carriers from crystal lattice defects.

Amorphous ionic matters

- $\gamma$  depends on structure and composition (inorganic glasses).



Macromolecular matters -  $\gamma$  depends mainly on production technology (hardeners residue, vulcanization, aging, ...).

### **Dielectric strength of insulators $E_p$**

One of basic characteristics of insulators. Insulator does not conduct electric current only up to certain intensity of el. field, after the limit has been exceeded, the current increases and voltage decreases

$E_p$  - dielectric strength,  $E_p = U_p / d$

$U_p$  - breakdown voltage,  $d$  – thickness of the insulator layer.

#### **Stages of electric breakdown:**

1. Initial stage – rapid increase of electric conductivity (various mechanisms).
2. Second stage – degradation of insulator after breakdown (permanent in solid insulators) depends on breakdown conditions (type of insulator, power output of the source).

### **Dielectric strength of gasses**

$E_p$  about one order of magnitude lower than dielectric strength of liquid and solid insulators.

Jump – shock ionization (free electrons) and photo-ionization.

Avalanche of electrons occurring due to shock ionization.

Discharge – secondary electrons created by ions falling on cathode.

Current density is caused external ionization.

The discharge takes place even without external ionization.

#### **Breakdown of gaseous insulators**

Breakdown character: purely electric breakdown. Breakdown occurs only after shock ionization and subsequent generation of avalanches of electrons (and positive ions).

#### Classification:

Non-independent discharge

1. type (external source of ionization),
2. type (emission of electrons from cathode).

The discharge.

### **Dielectric strength of liquid insulators**

Higher than strength of gasses, various jump mechanisms, resulting value depends on amount and character of impurities.

Discharge occurs at place with higher concentration of impurities.

Effect of electrode surface material.

High-purity liquids -  $U_p$  independent on pressure, time voltage exposure, main role of electrons.

Effect: solid impurities – decrease of  $U_p$ ,

gaseous bubbles –  $U_p$  depends on pressure,

dissolved (diffused) water -  $U_p$  depends on temperature.

### **Dielectric strength of solid insulators**

#### **Basic types of breakdown:**

- a) purely electric breakdown,
- b) thermal breakdown.

## 8.3 GASEOUS INSULATORS

### Properties of gaseous insulators

Their **low dielectric strength**, compared to solid and liquid insulators, is mainly caused by their low density. However, unlike other insulators, gaseous insulators are able to **regenerate** their dielectric strength. Dielectric strength of gases depends mostly on the distance between electrodes, temperature and pressure. It increases at high and low pressures; increased dielectric strength of gases is utilized in high-voltage cables, filled with compressed gas.

If the intensity of the electric field is low, the electric conductivity of gasses is low too. However amount of free electrons and ions can be substantially increased by ionization of neutral gas molecules, thus rendering the gas conductive. There are two kinds of gas conductivity – **non-intrinsic** and **intrinsic gas conductivity**. The difference is the process, by which the gas molecules gain the energy necessary for ionization. Non-intrinsic ionization of gas molecules is caused by an external source, e.g. by electromagnetic radiation. Intrinsic is caused by electric field which accelerates motion of charged particles enough so when they collide with neutral molecules and transfer its kinetic energy to them, the molecules gain sufficient energy to release one of their electrons.

Electric current conduction in gases is sometimes called **electric discharge**. There are several types of discharge. One of them is **corona**. It occurs in vicinity of very high voltage cables, if the intensity of el. field is sufficient to ionize the surrounding gas. Corona causes failures of very high voltage distribution network.

### Electric conductivity of gases

**Ionization** – physical process by which molecules and atoms produce electrons and positive ions (cations). Negative ions (anions) are formed by joining free electron and neutral particle. Due to secondary processes, the free charges can be captured by impurities (smoke, pollen, water drops and so forth).

**Shock ionization** occurs as a result of collisions of particles with sufficiently high kinetic energy to break away atom's electron (collision of  $\alpha$  or  $\beta$  particle and neutral molecule, more usually collision of molecule and electron, accelerated in electrical field).

**Photo-ionization** is caused by absorption of short-wave radiation (ultraviolet, roentgen or  $\gamma$  radiation); electron can thus gain sufficient energy to break away from the core.

**Thermal ionization** Requires specific gas condition to occur – high temperature or thermal radiation of heated gas.

**Discharges** can be divided to several groups:

**Glow discharge** occurs in strongly diluted gas ( $1 \div 100$  Pa). The discharge occurs at lower than ambient pressure; it is accompanied by light radiation of the gas (stimulation, non-elastic collision), current is very low, electrodes are cold.

**Arc discharge** occurs at pressures  $\sim 0.1$  MPa. It is intensively glowing discharge with clear borders of round shape with high current densities at low voltages.

**Plasma** – highly ionized gas ( $n^+ = n^-$ ).

Properties of plasma:

- high electric conductivity (similar magnitude to metallic conductors),
- high thermal capacity and conductivity,
- light emission source,
- affected by electric and magnetic field.

### Types of gaseous insulators:

#### Air

Air has relatively low dielectric strength which mainly depends on the shape of electric field, distance and shape of electrodes. Air is the **insulation of exterior distribution network**. It can also be utilized as **dielectric in capacitors**.

Physical properties:  $E_p > 100$  kV/mm, at 1 mm thickness it is only  $40 \div 60$  kV/mm, but decreases quickly with increasing humidity. It is thermally independent up to  $400 \div 450$  °C and then decreases.

## Nitrogen

has lower dielectric strength than air. It is used in mixture with inert gases, as **bulb** filling gas. Compressed nitrogen is used for **filling of high-voltage cables and capacitors**. Another application: **inert atmosphere** preventing oxidation of insulation oils in transformers, **cooling medium in cryogenics (super-conductors)**.

## Hydrogen

Gas with the highest thermal conductivity. Used for cooling of **large rotary machinery**. Its heat transport capacity is higher than that of air and thus increases efficiency of the device. Drawback is its flammability and that it forms explosive mixtures with air and also its low dielectric strength. Hydrogen is utilized as **filling gas for discharge lamps** and other devices, in electric furnaces as **reduction or reaction atmosphere**, also as **extinguishing agent in electric switches**, as **cooling and insulation gas in large rotary machinery** (synchronous compensators, flywheels), as **filling gas of some types of vacuum tubes**, in **semiconductor production** and others.

## Oxygen

is used in welding as oxidation environment. Air oxygen forms **ozone** during el. discharges.

## Inert gases He, Ne, Ar, Kr, Xe.

Do not react with other elements. Produced by fraction distillation of air. Application: lighting – **filling gas for lamps, light-bulbs** and various **discharge lamps**. Light-bulbs are filled with argon and krypton. Argon, neon, less often mixtures of these gases are used in **fluorescent lamps**. Xenon is used in **xenon arc lamps**.

## Vacuum and diluted gases

have high  $E_p$ . Quantum jump is facilitated by cold emission.

## Electronegative gases - fluorocarbons, chlorocarbons

Their molecules contain fluorine and chlorine atoms. Characteristic for their high dielectric strength  $E_p$  compared to air and nitrogen (up to 5 times more when compressed). Inflammable and thermally stable, non-toxic and chemically stable, application up to 220 °C. Drawback – SF<sub>6</sub> polluted with air and water decompose forming reactive products during discharge.

Electronegative gases **sulphur hexafluoride** and **freon** are used as **filling gases for transformers and high voltage switches**.

**Freon** (CCl<sub>2</sub>F<sub>2</sub>) - insulator, vacuum leaks seeker.

**Perfluorbutan** (C<sub>3</sub>F<sub>8</sub>).

**Sulphur hexafluoride** (SF<sub>6</sub>) – heavy gas. It is flammable, non-toxic, able to capture free electrons. Its dielectric strength is about 2.5 times higher compared to air (matches the liquid insulators at higher pressures). Excellent **electric arc extinguishing** properties (conducting areas of small diameter). Application: **cooling** (coolers, freezers), **extinguishing devices of high- and very high-voltage switches** (able to switch off hundreds of amperes currents magnitudes), **distribution substation encapsulation** (no need for revisions), **insulation filling of power cables and special transformers** (inflammable, explosive).

## **Metal vapors**

**Mercury rectifiers** are filled with mercury vapors, **sodium arc lamps** by sodium vapors.

## 8.4 LIQUID INSULATORS

Drain the surplus heat, fill the space, help extinguishing potential discharge and lighten the load on solid insulators. Main representatives are plant and mineral oils and synthetic liquids.

### Mineral oils

**Oil properties** from the gas solubility perspective – absorbs both water and gases, drawback: aging and oxidation.

Application: - power oil transformers, oil cables, high- and very-high voltage grommets, switches, capacitors.

**Mineral oils** are distilled from crude oil. Impurities containing oxygen are removed by refining. Properties of the oil correspond to its chemical composition.

**Transformer oils** – utilized in **transformers**, to keep them at temperatures where they provide favourable electrical properties. Viscosity and its thermal dependence are crucial. Another important attribute is **flash point**, i.e. lowest temperature, at which it can vaporize to forming a flammable mixture with air.

**Cable oils** – require the viscosity to be low after impregnation of the cable – the oil can therefore fill the cavities and saturate porous insulation (e.g. paper). Pure oil is not used for impregnation purposes – it is usually mixed with resin, forming oil compounds. The resin reduces the flow-down and prolongs the service life of insulation. Utilized mostly in **switches** to quickly **extinguish the arc discharge** which occurs during contact separation.

**Capacitor oil** – requires higher stability.

### Plant oils

Drying - **flaxseed oil** (electro insulating varnish).  
Non-drying - **ricin oil** (liquid dielectric, paper impregnation).

### Synthetic liquid insulators

**Polybutenes** - non-polar,  $\epsilon_r \sim 2.2$ ; tg  $\delta = 0.008$ , thermally stable  $E_p \sim 180$  kV/cm.

#### Silicon oils

- mineral oils (transformers, cables, capacitors),
- synthetic (chlorinated hydrocarbons, chlorinated biphenyles, silicon oils, fluorinated hydrocarbons).

Application: - **dielectrics for capacitors**, transformer filling (for higher temperatures),  
- **silicon grease**, **silicon rubber** (transverse bonds between O),  
- **oil for diffusion vacuum pumps** (vacuum technology).

**Synthetic liquids** – excellent insulation and dielectric properties. Non-flammable, non-explosive, highly stable and practically do not age. Esther based liquids represent large portion of the synthetic liquids. Chemically stable, withstands higher temperatures with excellent dielectric properties. Application: - **filling or impregnation for cables, film capacitors** and others.

- Chlorinated biphenyles, e.g. **pentachlorobiphenyle**. **Harmful**.
- Fluorinated hydrocarbons, non-polar and excellent dielectric properties.

**Electrolytes** – liquids or sometimes solids, el. conductive. Solutions of molecules formed by reaction of two opposite polarity ions. Current conduction causes transport of mass from anode to cathode. This is utilized in **galvanic metal coating**, **electrolysis** (decomposition by electric current), **galvanic cell** – both primary and secondary and in **electrolytic capacitor**.

**Varnish** is a solution of film-forming compounds (natural or synthetic resin, drying plant oils and asphalt) in organic thinner. Varnishes are divided in groups by their chemical composition:

- natural resin,
- alcohol varnish,
- drying oil – oil varnish,
- synthetic resin – synthetic varnish.

Classification

- **Drying oil varnish** – **protection against exterior influences**.
- **Phenol formaldehyde varnish** – **saturation of coil wiring**.

- *Polyamide varnish* – conductor insulation, absorbs moisture.
- *Polyester varnish* – glyptal, alkyd and terephthalate varnish.
- *Thinner-less varnish* – vacuum pressured coil impregnation.
- *Epoxide varnish* – conductor insulation, impregnation and gluing of components.
- *Polyurethane varnish* – conductor insulation, soldering without removing the insulation.
- *Silicon varnish* – low dependency of electro-insulating properties on temperature.
- *Polyamide varnish* – resistant up to 220 °C.
- *Acrylate varnish* – conductor insulation.

## 8.5 SOLID INSULATORS

### 8.5.1 SOLID INORGANIC INSULATORS

Main inorganic insulators are mica, asbestos, ceramic and glass. Most solid inorganic insulators are silicate based. The building block of their structure is silicon – oxygen group with very strong chemical bond.

TECHNICAL APPLICATIONS OF SOLID INORGANIC INSULATOR:

- construction purposes – high resistivity, dielectric and mechanical strength,
- capacitor dielectrics for el. charge storage, high permittivity and dielectric strength,
- electro-mechanic resonators,
- electrostriction pressure components (piezoelectric effect).

### MICA

Crystalline mineral which, thanks to its layered structure, easily chips to form very thin leaves. Stable even at high temperatures and in many chemical substances. Mica is characterized by having very good dielectric and chipping properties, elasticity, and high thermal resistance. Mica is found in nature in many kinds however only several are utilized for technical applications:

**MUSCOVITE** – potash mica

**PHLOGOPITE** – magnesium mica

Crude mica is suitable for pads for electric heated and regulation resistors. Chopped mica (thickness of 0.05 to 0.45 mm) is utilized for production of multi-layered insulators **MICANITE**, **MICACOIL** and **MICA STRIPS**. Mica exhibits low dielectric losses; dielectric strength depends on the thickness of layer. The dielectric strength increases with decreasing layer thickness. Dielectric strength of muscovite is higher than that of phlogopite. Maximum operation temperature of muscovite is 600 °C, resp. 900 °C for phlogopite.

Mica waste processing technology produces elastic, electro-insulation material in form of a foil called **REMICA** – mica waste and least valuable ore constituents are processed – production of **multilayered insulators**.

**Application of mica in electrical engineering:**

- dielectrics in capacitors, material for insulation desks (micanite, mica folium), strips, electrode bearing systems and heating wires,
- milled mica with low-melting glass is utilized for pressed insulation (micalex). It is also utilized in HF technology at high temperatures. It has excellent properties for use in electrical engineering, including HF and vacuum technology.
- micanite with bonding agent is used for production of commutators; board- or foil-shaped mica is used for production of heating wires (micafolium and mica strip).

**MICANITES** are fabricated from mica strips glued together by a bonding agent (shellac, epoxide) on a substrate – typically fibre glass, paper.

Hard micanite (commutator) – insulation of commutator lamels.

Elastic micanite – partially hardened bonding agent – commutator cuffs, slot insulation.

**MICAFOLIUM** two layers of strips on elastic substrate, sticky surface – wrapping and ironing of high-voltage coil insulation.

**MICALEX** – milled mica waste with glass bonding agent – construction and insulating material.

**ASBESTOS** is non-flammable, hygroscopic. High dielectric losses and low dielectric strength up to 300 °C. It is known **carcinogen**. Utilized for production of ligaments, fabric, paper and others. **Chrysotile and crocidolite asbestos** are utilized as an **insulation material** for electrical engineering.

- Properties:** - low dielectric strength,  $\rho \sim 10^8 \Omega \cdot m$  (enhanced by impregnation), high thermal resistance.
- Application:**
- thread for **conductor wrapping**,
  - combined with **fibre glass**,
  - fabrics, strips,
  - paper – combined with glass fabric,
  - asbestos concrete – **extinguishing chambers of switches**, boards, pipes.

**Note: Careful!** Nowadays practice application of asbestos is very limited due to its health hazard issues.

## **CERAMIC MATERIALS**

Ceramic typically has good electro-insulation properties, its properties are time-stable and it has good resistance against high-temperature, temperature-shock, chemicals, exterior conditions and humidity. Ceramic has very high **hardness**, and is usually **brittle**. Its **compressive strength** is usually one order of magnitude higher than its tensile strength. Considering the **constriction** caused by firing, it is difficult to produce dimension-precise products without further working - grinding.

**Kaolin** and **clay** are the raw materials for production of silicate ceramics such as **pottery, earthenware and mullite ceramics**. e.

- Chemical composition:**
- silicate ceramics:  $SiO_2$  + mixture of metal oxides,
  - non silicate ceramics:  $TiO_2$ ,  $BaTiO_3$ ,
  - oxide ceramics:  $Al_2O_3$ ,  $MgO$ ,  $BeO$ ,
  - non oxide ceramics: hard and resilient (carbides, nitrides, silicides etc.).

### **Types of ceramics – basic classification by application:**

1. Ceramic materials for power industry electrical components: **POTTERY** – up to 1100 °C, **HARD POTTERY insulators and grommets for transformers**; **STEATITE** – similar to pottery, slightly better, **EARTHENWARE** – worse than pottery, hygroscopic, needs to be glazed, application for **large insulators**. **HARD POTTERY** is very little hygroscopic, nonporous, thermally stable, impervious for water and gases. Application: **electric wiring insulators, grommets for transformers**. Not suitable for high-frequency applications.

2. Ceramic materials for high-frequency (HF) technology:

**STEATITE** surpasses the pottery in homogeneity of its structure. It has better electrical properties and mechanical strength even at higher temperatures. Application: **electro-thermal devices, measurement devices, relays, contactors, HF technology** for low dielectric losses, **coil frames, vacuum tube components**, replacement of high-quality pottery in **electro-thermal and measurement devices**.

3. Ceramic materials for components operated at elevated temperatures and temperature-shock resistant components:

**MAGNESIUM EARTHENWARE, CORDIERITE CERAMIC, MAGNESIUM POROUS EARTHENWARE, MULLITE CERAMIC, OXIDE CERAMIC, BERYLLIUM CERAMIC, ZIRCONIUM CERAMIC, CORUNDUM CERAMIC**. Magnesium porous earthenware – **bearings of resistive wires, heating wires** of appliances up to 1100 °C), mullite ceramic (components for temperatures above 1300 °C), corundum ceramic (hard, tough) – **insulators, resistor frames, integrated circuits pads**.

**EARTHENWARE** has worse properties than pottery, it is hygroscopic, needs to be glazed- fabrication of **large insulators**.

**MAGNESIUM EARTHENWARE** - application up to 600 °C.

**CORDIERITE CERAMIC** - high temperature-shock resistance, resistant in discharge arc, unsuitable for HF.

**RUTILE CERAMIC** (ferroelectric ceramic) has good dielectric properties. Application: **miniature capacitors for HF**.

**OXIDE CERAMIC** – breakdown time  $\sim 10^{-8}$  s, very high temperatures (above 2000 °C) applications (beryllium, zirconium, periclase, lithium and corundum  $Al_2O_3$  ceramic), diamond working. Application: vacuum sealed **casings of transmission vacuum tubes, pads of integrated circuits**.

#### 4. Ceramic for capacitors:

**RUTILITE, STABILITE** and **PERMITITE** – materials with either linear or non-linear relationship between  $\epsilon_r$  and temperature  $T$ . Commercial brand name of titanates: **PERMITITE**.

**GLASS** is **amorphous inorganic material** (super-cooled liquid). Ions of additives ( $\text{Na}^+$ ,  $\text{K}^+$ , and others.) modify various properties of glasses such as melting point, strength, brittleness, colour and electrical properties.

Technical glass belongs to the group of materials which do not solidify at specific temperature due to crystallization like metals, rather can be super-cooled below this point. Favourable attributes of technical glass is **good hot formability, good electrical, thermal and chemical properties, that it is impervious for gasses and can form vacuum tight seals with metal.**

##### Physical properties of glass

Temperature dependency of viscosity corresponds to the production technology and subsequent working of the glass.

Considerable thermal and chemical resistance.

Optic properties – refractory index, reflection.

Vacuum tight.

**Mechanical properties of glasses** correspond to the state of the surface and also temperature (expansivity).

Glass is **brittle**, can better withstand pressure than tensile stress.

Glass fibres have high tensile strength.

##### Electric properties of glass

Depends on chemical composition and operation conditions. **Ionic** type electric conductivity. **Dielectric strength** of glass is, compared to other insulators, high:  $E_p \sim 200 \div 400 \text{ kV}\cdot\text{cm}^{-1}$ , however it is much lower in practice. Glass is strongly polar,  $\epsilon_r = 3.7$  (pure quartz glass) to  $\epsilon_r = 16.5$  (lead glass) or even more.

##### Types of glass and their application

In electrical engineering, glass is mostly used for insulation and construction purposes, e.g. **light bulbs, discharge lamps, fluorescent tubes, vacuum tubes, displays** and other vessel shapes for electrodes kept in vacuum, gases or vapors.

**Quartz glass** low losses – 99.9 %  $\text{SiO}_2$ , transparent or opaque, good thermal properties.

Application: **coil frames for HF technology, vessels and cases for discharge lamps and rectifiers.**

**Boron-silicate glass (hard glass)** – many kinds with good electric properties (**SIMAX**) – utilized in **HF electrical engineering, tungsten, molybdenum and covar seals**. Suitable for optic fibre production for **light guides**, production of **PCB** (printed board circuit) by joining glass fabric by epoxide, silicon, in **microelectronics** (substrate for thin layers) and others.

**Lead glass (soft glass)** – **receiver vacuum tubes, necks of TV screen tubes.**

**Alkali glass (MgO)** – easy meltable, can not withstand rapid temperature changes - **lighting, screens, insulation (fabrics, lamination, glass insulators).**

**Special glass** – hardened, sintered, electric conductive glass (cermet potentiometers), magnetic glass, for **vapor deposition from vacuum, conductive glass, glass solder.**

**Glass fibre** fabricated from **Eutal** by drawing a wire from melt liquid in Pt crucible, diameter  $\sim 5 \div 10 \mu\text{m}$ , 100  $\div$  200 fibres. Fibres are then processed to produce thread, cord or fabric.

Application: light guides, fibre optics (telecommunications), impregnation.

**Insulation glass** thermally - insulating, soundproofing.

## 8.5.2 SOLID ORGANIC INSULATORS

### High-molecular insulators

#### Classification:

- a) origin
  - natural,
  - natural based,
  - synthetic (plastic).
- b) state
  - solid,
  - liquid.
- c) chemical composition
  - carbon string,
  - silicon -Si-O-,
  - hetero-atomic string.
- d) monomer molecule shape
  - linear,
  - branched,
  - cross-linked, planar or spatial.
- e) thermal effects
  - thermoplastics,
  - thermosetting polymers,
  - elastomers.
- f) processing technology
  - mechanical machining,
  - shaping (pressing, extrusion, injection, blowing),
  - casting and moulding,
  - other technologies.
- g) storage and manipulation
  - natural shape (wood, resin, oils),
  - semi-finished products for machining and shaping (boards, rods),
  - raw materials (powders, granule, cast resin).

**ORGANIC INSULATORS.** For example both natural and synthetic oil, wax, asphalt, drying oil, natural resin, natural rubber, plastics, varnish, fibrous and layered insulator.

Organic insulators are, in most cases, essentially macromolecular compounds; building units (monomers) are connected in periodic manner to form macromolecule (polymer). Chemical structure of the macromolecule determines its electrical, mechanical and chemical properties, as well as their thermal resistance.

The configuration of monomer molecules in macromolecule can be:

- **linear.**
- **branched,**
- **spatial.**

## 1. ORGANIC INSULATORS BASED ON NATURAL MACROMOLECULAR MATERIALS

### 2. SYNTETIC ORGANIC INSULATORS - classification

- a) **THERMOSETTING POLYMERS (THERMOSETS)**
- b) **THERMOPLASTICS**
- c) **ELASTOMERS**

### 3. **VARNISH**

## ORGANIC INSULATORS BASED ON NATURAL MACROMOLECULAR MATERIALS

Solid insulators produced from natural macromolecular materials can be of both the animal (shellac, silk) or plant origin (wood, cotton, natural rubber), but also can be produced by processing of natural raw materials (cellulose, paper, elastic rubber).



## A) NATURAL RESIN

produced by either biological processes of certain animals or in resin producing plants. Natural resin can be, based on their age, divided to recent (produced recently) and fossil (preserved underground from prehistoric times).

**SHELLAC** is a resin of natural origin. Shellac is based on esters of fatty acids. At 60 °C, shellac becomes elastic and continues to soften up until 90 °C where it starts to melt. During electric breakdown, the shellac does not create conductive paths, but increases its resistance, similar to e.g. **micanites**. Its good electric properties and adhesive force are utilized in electrical engineering for production of **adhesive (insulator) varnish**, necessary for micanite and micafoil production and also as **binding agent in mica insulator production**.

**ROSIN** is produced from resin of coniferous trees. Softening temperature is about 60 °C - it is further increased by air oxidation; the solubility in mineral and plant oils, alcohol, petrol, turpentine and acetone decreases. Utilized in cable industry for production of **cable impregnation materials**, raw material for **electro-insulating varnish** production and for production of **fluxes for soft solders**.

**COPAL** - fossil or fresh resin produced from tree secretion. **Added to oil varnish** for lacquer film hardening and sometimes also as a replacement of shellac.

**AMBER** is the hardest fossil resin with excellent electric properties. Used as **contact insulation of highly sensitive measurement devices**. When rubbed, it exhibits electrostatic properties. **Best available insulator**. Its resistivity is very high ( $10^{16} \Omega \cdot m$ ) and it is stable even in humid environment.

## B) FIBROUS INSULATING MATERIALS

Organic fibrous insulators are important not only for their good electrical and mechanical properties, good workability – it can be shaped into cylindrical components. Main drawback is its hygroscopicity caused by its high porosity, unless they are sufficiently impregnated.

Natural fibrous materials are wood and cotton. Synthetic are paper, cardboard and fabric products. Main raw material for their production is plant fibre either from wood or cotton, flax and others. The main component of these materials is cellulose.

**CELLULOSE** is the main component of plant fibre. Cellulose is insoluble in water, diluted acids, alkalis and organic thinners. Processed cellulose is the basic material for production of electro-technical papers.

**ELECTRO-TECHNICAL PAPER** is fabricated from cellulose, produced by boiling wood splinters in lye solution, washing and milling. Resistivity of electro-technical paper is very high, however its dielectric strength is low. Dielectric strength depends on the structure, density, surface and thickness. The paper is usually impregnated with natural mineral wax (paraffin or mineral oil). In electrical engineering, the paper is used as **dielectric in foil capacitors**, as an **insulation of power and telecommunication cables**, as **insulation of transformer wiring**. **Electrolytic capacitor** uses the paper as the substrate for the electrolyte. This material is used for production of **layered insulators** (laminated papers) and other combined insulators.

Types of paper:

1. **Paper for power cables** (wrapping of power and telecommunication cables).
2. **Paper for telecommunication cables**
3. **Paper for wiring insulation in oil transformers**.
4. **Paper for hardened insulators**.
5. **Varnished insulator papers** (layers between coil wire layers).
6. **Paper capacitor dielectrics** – as thin as possible (5 to 25  $\mu m$ ), high dielectric strength (to 40 kV/mm) and high density.
7. **Polyamide paper** (pad for production of **conductors and cables, coil frames**).
8. **Laminated and varnished papers**.

**CARDBOARD** is produced by joining layers of paper. Classification:

*common,  
grooved,  
for transformers.*

## FABRIC INSULATION MATERIALS

**Yarn** is used for **coil wiring wrapping, insulation of flexible telephone cables**. There are several kinds of yarn, namely cotton yarn, silk yarn and also yarn from synthetic fibres.

**Fabric** is impregnated with insulation varnish to enhance their electric properties.

**Glass fabric**

**Plating of electro-insulation material** – materials strongly joined with metallic, typically copper foils (**cuprex card, cuprextit**) – for **production of printed circuits**.

## **SYNTHETIC ORGANIC INSULATORS**

Largest group of insulators used nowadays in electrical engineering. They have better properties than natural organic insulators and can be easily produced in desired amounts and quality. Divided to several groups based on effect of heating: **thermosets, thermoplastics and elastomers**.

### **1. THERMOSETTING POLYMER (THERMOSET) – thermally hardenable material**

Thermosets have spatial structure, do not soften after repeated heating but it can cause their destruction. They are produced as pressings, semi-finished products (boards, tubes and rods from hardened tubes and paper), potting resin, glues and varnishes for electrical engineering, mechanical engineering and consumer industry. Thermosets are processed by pressing, casting and injection. This group is represented by some types of phenol formaldehyde resins, melamine resins, Umakarts and epoxides, based on the kind of used resin, filler and poly-condensation process (hardening).

**PHENOL FORMALDEHYDE RESINS**: phenol + formaldehyde – poly-condensation. Shrinkage of the castings is crucial. Common phenol formaldehyde resin is **BAKELITE**. Bakelite has always dark-brown or black colour and darkens on light. Bakelite is usually pressed in mixture with other additives, e.g. wood or stone flour, fabric fibre etc. Bakelite is used for products which are needed to have good thermal, fire and chemical resistance.

**MELAMINE RESINS** – colour-less, transparent synthetic resins. Formaldehyde + melamine – poly-condensation. Eddy current resistant, suitable for very high voltage applications, thermal resistant. Example: layered melamine resin **UMAKART** (brand name).

**EPOXIDE RESINS** are produced by poly-condensation, hardened by polymer addition. Exhibit low hygroscopy, low shrinkage and good insulating properties. Mixtures for potting and moulding are two- or three-component - hardening agent is Eposine. Epoxide glues have an excellent adhesion. Application: impregnation and gluing varnish, abrasive resistant, glues (thermosets, metals and trafo-sheets gluing), casting resin + fillers, production of construction components, fibreglass.

**POLYESTHER BASED THERMOSETS** Application: bonding agents of layered materials, casting and potting resin, surface and impregnated varnish, fibreglass, **connectors, coil frames for resistor wiring**.

**LINEAR POLYURETHANES** – fibre forming materials, polyamide replacement, oriented foil. Application: cable coating, insulation varnish, glue, foam materials, polyurethane rubber.

### **2. THERMOPLASTICS**

This is a group of plastics which, subjected to heat, soften; they recover their former properties when cooled. Exceeding the fusion temperature results in decomposition of thermoplastic material. Their dielectric properties at various frequencies, temperatures and humidity levels must be measured, if they are utilized for electrical engineering purposes.

**POLYSTYRENE (PS)** is amorphous, glass-like material. It is non-polar, its molecules have small dipole moment. It relatively good light conductor, it has low thermal resistance (-30 to +70 °C), and starts softening already at 85 °C. Polystyrene is used for production of **injected mouldings** (e.g. device covers). Polystyrene is typical insulator for **high-frequency purposes**. It is used also for **coaxial cable jacks**, various **construction components of measurement devices** and others.

**Oriented polystyrene film (Styroflex)** - **dielectrics of foil capacitors** or **insulation of HF cables**.

**Foam polystyrene materials** - casings (eventually casing fillers) for appliances.

**POLY(METHYL METHACRYLATE)**: polyester of acrylic acid, transparent for UV light– **DENTACRYLE** (brand name), material for moulds.

**POLYAMIDE** – **conductor insulation in dry environment**. Fibres (**SILON, NYLON**). Application: cogwheels, ball bearings, crystalline thermoplastics.

**POLYFORMALDEHYDE** chemically resistant, welded joints. Application: **cogwheels in HF applications, flexible pens, flat springs**.

**POLYCARBONATES**: high ionization resistance and high dielectric strength, low hygroscopicity, can be filled with glass fibre, similar strength as carbon alloys. Application: mechanically, **electrically and thermally stressed shaped casings, insulation foils of substrates, capacitor dielectric.**

**FLUOROPLASTICS** - polyethylene with hydrogen atoms replaced with fluorine, very good electro-insulating properties, thermal conductivity, good formability, brand names **TEFLON, TEFLEX**. Fluoroplastics are used for special applications, in chemical industry and HF electrical engineering.

**Polytetrafluorethylene (PTFE) = TEFLON** is non-polar insulator with extraordinary properties. Its relative permittivity  $\epsilon_r$  does not exceed 2.2; loss factor  $\text{tg } \delta = 1 \div 2 \cdot 10^{-4}$  is frequency, temperature and humidity level independent, completely non-hygroscopic. Very wide allowable operation temperature range: from  $-70$  °C to  $+250$  °C. Softens above  $327$  °C. It is chemically stable, attacked only by fluorine and melt alkali metals. Good sliding properties. Application: **Demanding conductor insulation, Teflon ball bearings.**

**Polychlorotrifluoroethylene = TEFLEX** is slightly polar. Stable in temperature range of  $-70$  to  $+140$  °C. Liquid teflex is used in **transformers** or for **paper capacitor impregnation.**

**POLYVINYLCHLORIDE (PVC)** - polar, can not be used for HF applications, temperatures up to  $60$  °C. PVC starts softening at around  $85$  °C. Further temperature increase ( $180$  °C) causes it to decompose; carbonizes in flame.

**Rigid PVC (NOVODUR, VINIDUR)** Production of boards, tubes armatures - for chemical device production.

**Plasticized PVC** replaces rubber materials in production of **conductor and cable insulation**. It is not necessary to plate the conductors with tin. **Power cables** with PVC insulation for application up to  $10$  kV are produced commonly. Also used for hoses.

**Thermoplastics produced from natural macromolecular materials** Cellulose acetate replaced natural silk. Application: **wrapping material**, tags, scales, boards.

**POLYETHYLENE (PE)** has excellent resistance against chemicals, vapors and gases. Non-flammable types - chlorinated PE and sulfochlorinated PE have been developed. Used as **conductor insulation**, for **cable covers** and other **insulation parts**. In HF engineering as **coaxial cable insulation, telecommunication cable and conductor insulation**. Insulation from foam polyethylene is becoming very important; it has  $\epsilon_r \approx 1.5$  (i.e. the conductor has lower capacity and is also lighter).

**POLYPROPYLENE (PP)** – very similar electrical and chemical properties as polyethylene.

### 3. ELASTOMERS

Substantial part of insulation of all conductors. Basic attribute of all elastomers is their high flexibility. They can be, at room temperature and reasonable load, elongated to double their length; they quickly return to its original dimensions if the stress is relieved. Vulcanization of elastomers enhances their properties. Most important elastomers are natural rubber and rubber. Utilized as **seals, insulation grommets, dampening components and construction parts, eventually as potting material for electronic circuits.**

#### RUBBER

Rubber can be vulcanized by addition of sulphur or sulphur compounds. This enhances its tensile strength, flexibility and also thermal, chemical and mechanical resistance. However, rubbers easily oxidize, e.g. by ozone which results in quick deterioration of mechanical properties – aging.

**Natural rubber** is produced from latex of some tropical trees (Hevea brasiliensis). Ultraviolet light causes quick aging of rubber, facilitated by photochemical oxidation. Rubber rapidly loses its elasticity and becomes insoluble and brittle. **Elastic gum** is produced by mixing and vulcanization of rubber. Elastic gum is used for production of **cable insulation**, its drawback is low thermal resistance.

**Synthetic rubber** produced from acetylene, benzene other compounds from crude oil, natural gas or coal.

**Butadiene rubber** – thermal vulcanization at  $200$  °C without sulphur. Application: - **cable insulation.**

**Styrene-butadiene rubber** - elastic, chill-resistant. Application: **insulation of cables, conductors** (increased resistance at low temperatures).

**Chloroprene rubber** – **strongly stressed insulation.**

**Silicon rubbery**: good el. properties, high thermal resistance (up to  $180$  °C), chemical stability, hydrophobic. Application: **insulation of thermally-stressed cables, capacitor and transformer potting material.**

## NATURAL WAX AND COMPAUNDS

Natural waxes are complex organic (animal or plant) compounds. Waxes are utilized in electrical engineering either solely for **impregnation of fibre insulators** or as a part of **potting mixtures**, eventually as **electro-insulating varnish additive**.

**Non-polar waxes (paraffin, ozokerite and ceresin)** have very low relative permittivity, low dielectric losses factor and high resistivity.

**Paraffin wax** Application: **capacitor insulation** for low voltages with paper dielectric, operated at temperatures under 55 °C and as **component of insulation materials** of fabric **cable coating**.

**Ozokerite** is utilized in **cable industry**. Processed to compaunds used in production and cable joining.

**Ceresin** is used as impregnation agent or additive to other materials to enhance their resistivity, potting material for **surface treatment of radiotechnic transformers**, **low power capacitors and cable terminals**.

**Bee wax** is used in combination with paraffin for **impregnation of low power conductors wrapped in cotton**, **gluing of coils for HF technology** and as component of various plastic compounds.

**Montan wax** – **potting and impregnation of components in radio technology**.

**Carnauba wax** – added to other waxes to enhance their hardness and softening temperature.

**Plastic compaunds** - solid mixtures of bitumen, asphalts, waxes, resins or even oils without volatile thinners. Used as **potting materials** without any thinners or other volatile matters and are able to fill empty spaces in insulation systems. Prevent ionization of air in the cavities and penetration of humidity to fibre, combined and **layered insulators** or **whole insulation systems**.

## ASPHALTS AND BITUMENS

Amorphous materials - mixture of hydrocarbons and lower amounts of oxygen and sulphur. At low temperatures, these materials are hard and brittle developing clam-shell-like cracks. Not soluble in water. Utilized as **potting or filling material**. Asphalts and bitumens are suitable for application in **power electrical equipment**. Utilized for **emptying** the **capacitor vessels**, potting of **grommets** and fabrication of **cable terminals**. Their main purpose is protection of electro-technical components or joints of cables against aerial and ground humidity. Nowadays replaced by plastics.

## 8.6 DIELECTRICS AND CAPACITORS

Capacitor is one of basic components for electrical engineering, its main attributes are capacity  $C$  [F] (common capacitors have capacity in magnitude of pF to  $\mu$ F), loss factor  $\text{tg } \delta$  and rated voltage [V].

Capacitates are utilized in electronic circuits **coupler component between circuits**, **in tuned circuits**, **HF filters**, **smoothing of rectified voltage in sources** and mainly **for compensation of reactive components in alternating electric networks and start-up of some induction motors**. Capacity, rated voltage and dimension are the basic attributes for correct capacitor selection. The capacity is directly proportional to the relative permittivity  $\epsilon_r$  of dielectric, are two overlapping electrodes and inversely proportional to the distance between the electrodes. Distance between electrodes corresponds to the thickness of dielectric.

### TYPES OF CAPACITORS

**SOLID** capacitors (Fig. 8.1) consist of two metal electrodes separated by thin layer of dielectric. Solid capacitors can be classified by the type of utilized dielectric material:

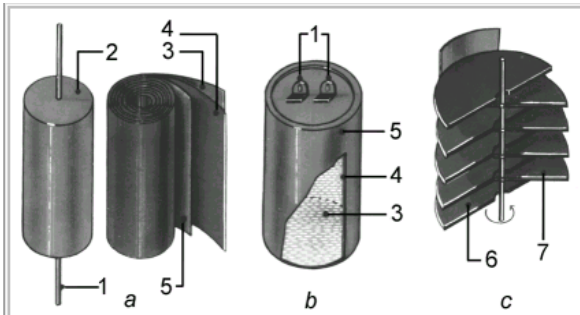
- air,
- with paper dielectric,
- metalized paper,
- plastic foil,
- mica,
- ceramic (or glass),
- aluminum electrolytic,
- tantalum electrolytic,
- varicap.

### **ADJUSTABLE:**

- tuning,
- trimming.

**SMD** surface mount device technology:

- ceramic,
- mica multilayered,
- electrolytic,
- tantalum.



**Fig. 8.1** Examples of basic capacitor types a) foil capacitor; b) electrolyte capacitor; c) air rotary capacitor; 1 terminal, 2 casing, 3 and 5 electrode, 4 dielectric, 6 solid electrode, 7 rotary electrode

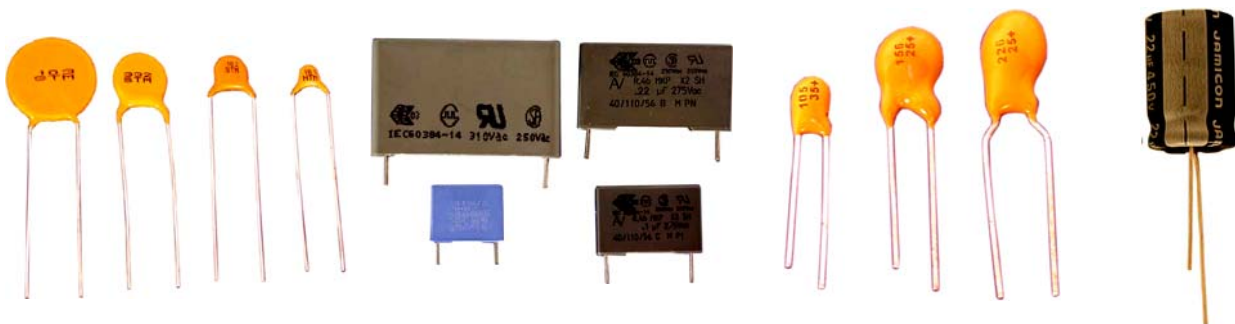
### **Ceramic capacitor**

This is the type of capacitor most widely used in electronic devices. High stability of ceramic capacitors is mainly caused by heterogeneity of ceramics. Dielectric constant of these components is around  $\epsilon_r = 10$  (pure aluminum oxide  $\text{Al}_2\text{O}_3$ ) up to  $\epsilon_r > 10000$  (e.g.  $\text{BaTiO}_3$ ).

Ceramic capacitors are mostly utilized in **HF engineering**. The dielectric is usually titanium, zirconium or tin oxides, in technical practice called **STABILITE, STEATITE, RUTILITE** and **PERMITITE**. These capacitors have high capacity and miniature dimensions.

### **Most common types of ceramic capacitors:**

- disc capacitors,
- desk soldered directly to copper conductor,
- flat,
- tube,
- grommet comprising of ceramic tube.



a) ceramic

b) foil

c) tantalum

d) aluminum

**Fig. 8.2** Various construction designs of commercially produced capacitors - c) and d) types are electrolytic

### **Plastic foil capacitors**

Dielectric material is usually polyester, polypropylene or **styroflex** in form of thin foil of 5 to 20  $\mu\text{m}$  thickness. Capacitors are characteristic for their high dielectric strength, low loss factor and high insulation resistance. They are therefore suitable for application in **circuits with oscillators**. They are also used in **HF circuits** and non-induction implementation as **blocking capacitors**.

### **Aluminum electrolytic capacitors**

Aluminum electrolytic capacitors have typically capacity above 1  $\mu\text{F}$  and need to be sufficiently small. Dielectric is a layer of  $\text{Al}_2\text{O}_3$  forming on positive electrode. The electrode has, even in very thin layer, relatively

good insulation ability. The rule is: thinner the dielectric, higher the capacity of the capacitor. Electrolyte has past-like consistency. Electrolytic capacitors are utilized in **power circuits** and circuits without parasitic induction issues. Bipolar aluminum electrolytic capacitors are also utilized for example in **asynchronous motors** as **start-up capacitors**.

### **Tantalum electrolytic capacitors**

Typical for their low passing current, lower parasitic inductance, higher time and temperature stability and lower losses in acoustic spectrum. Produced in miniature design - Fig. 8.2 c) and for lower voltages than aluminum capacitors. However polarity change causes permanent breakdown!!!

**Super-capacitor** also called **Gold cap**, is special small capacitor with capacity of 0.1 F to 1 F. This high value is achieved by implementation of special porous electrodes. Cannot be charged or discharged by strong currents since current stronger than few mA damages the capacitor. Fabricated typically for voltage around 5 V. These capacitors replace NiCd accumulators utilized as source for CMOS components.

### **Capacitors for alternating voltage**

For alternating voltage applications, all types of foil and ceramic capacitors can be used. These capacitors use mineral and silicon oils as the dielectric material; these oils can withstand high temperatures and have excellent dielectric properties. Capacitors in alternating circuits provide **power factor compensation in substations** and for **startup of single-phase motors**.

### **Varicap**

Varicaps are one kind of adjustable, semiconductor based capacitor. Utilized in **tuning circuits, automated frequency circuits, in modulation circuits for frequency modulated transmitters** and others. They utilize the fact that each PN junction has certain capacity which changes with polarization voltage put on the junction terminals. Commonly available varicap types have capacity of 2 to 15 pF (types for very-high-frequency circuits) or 12 to 250 pF (tuning circuits up to 30 MHz) for voltage changes between 1 to 30 V.

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