Unit-III: Preparative Methods in Solid State Chemistry

Exprimental Procedures

The Ceramic Method

The simplest and most common way of preparing solids is the ceramic method, which consists of heating together two non-volatile solids which react to form the required product. This method is used widely both industrially and in the laboratory, and can be used to synthesize a whole range of materials such as mixed metal oxides, sulfides, nitrides, aluminosilicates and many others—the first high-temperature superconductors were made by a ceramic method. To take a simple example we can consider the formation of zircon, $ZrSiO_4$, which is used in the ceramics industry as the basis of high temperature pigments to colour the glazes on bathroom china. It is made by the direct reaction of zirconia, ZrO_2, and silica, SiO_2 at 1300°C:

$$ZrO_{2(s)}+SiO_{2(s)} \longrightarrow ZrSiO_{4(s)}$$

The procedure is to take stoichiometric amounts of the binary oxides, grind them in a pestle and mortar to give a uniform small particle size, and then heat in a furnace for several hours in an alumina crucible.

Sealed Tube Methods

Evacuated tubes are used when the products or reactants are sensitive to air or water or are volatile. An example of the use of this method is the preparation of samarium sulfide. In this case, sulfur has a low boiling temperature (717 K) and an evacuated tube is necessary to prevent it boiling off and being lost from the reaction vessel. The preparation of samarium sulphide, SmS, is of interest because it contains samarium (a lanthanide element) in an unusual oxidation state +2 instead of the more common state +3. Samarium metal in powder form and powdered sulfur aremixed together in stoichiometric proportions, and heated to around 1000 K in an evacuated silica tube. (Depending on the temperature of reaction, pyrex or silica are the common choices for these reaction tubes, as they are fairly inert, and can be sealed on to a pyrex vacuum system for easy handling.)

The product from the initial heating is then homogenised and heated again, this time to around 2300 K in a tantalum tube (sealed by welding) by passing an electric current through the tube, the resistance of the tantalum providing the heating. The pressures obtained in sealed reaction tubes can be very high, and it is not unknown for tubes to explode however carefully they are made; it is thus very important to take safety precautions, such as surrounding the tube with a protective metal container, and using safety screens.

Spray-Drying

The reactants are dissolved in a suitable solvent and sprayed as fine droplets into a hot chamber. The solvent evaporates leaving a mixture of the solids as a fine powder which can then be heated to give the product.

Freeze-Drying

The reactants are dissolved in a suitable solvent and frozen to liquid nitrogen temperatures (77 K). The solvent is then removed by pumping to leave a fine reactive powder.

Co-Precipitation and Precursor Methods

At a simple level, precursors such as nitrates and carbonates can be used as starting materials instead of oxides: they decompose to the oxides on heating at relatively low temperatures, losing gaseous species, and leaving behind fine, more reactive powders. An even more intimate mixture of starting materials can be made by the co-precipitation of solids. A stoichiometric mixture of soluble salts of the metal ions is dissolved and then precipitated as hydroxides, citrates, oxalates, or formates. This mixture is filtered, dried, and then heated to give the final product. The precursor method achieves mixing at the atomic level by forming a solid compound, the precursor, in which the metals of the desired compound are present in the correct stoichiometry. For example if an oxide MM′2O4 is required, a mixed salt of an oxyacid such as acetate containing M and M′ in the ratio of 1:2 is formed.

The precursor is then heated to decompose it to the required product. Homogeneous products are formed at relatively low temperatures. A disadvantage is that it is not always possible to find a suitable precursor, but the preparation of barium titanate gives a good illustration of this method. Barium titanate, BaTiO3, is a ferroelectric material widely used in capacitors because of its high dielectric constant. It was initially prepared by heating barium carbonate and titanium dioxide at high temperature.

$$\mathrm{BaCO3(s)+TiO2(s)} \longrightarrow \mathrm{BaTiO3(s)+CO2(g)}$$

However, for modern electronic circuits, it is important to have a product of controlled grain size and the precursor method is one way to achieve this. The precursor used is an oxalate. The first step in the preparation is to prepare an oxo-oxalate of titanium. Excess oxalic acid solution is added to titanium butoxide which initially hydrolyses to give a precipitate which then redissolves in the excess oxalic acid.

$$\mathrm{Ti(OBu)_{4(aq)} + 4H_2O_{(l)}} \longrightarrow \mathrm{Ti(OH)_{4(s)} + 4BuOH_{(aq)}}$$
$$\mathrm{Ti(OH)_{4(s)} + (COO)_2{}^{2-}{}_{(aq)}} \longrightarrow \mathrm{TiO(COO)_{2(aq)} + 2OH^{-}{}_{(aq)} + H_2O_{(l)}}$$

Barium chloride solution is then added and barium titanyl oxalate precipitates.

$$\mathrm{Ba^{2+}{}_{(aq)} + (COO)_2{}^{2-}{}_{(aq)} + TiO(COO)_{2(aq)}} \longrightarrow \mathrm{Ba[TiO((COO)_2)_2]_{(s)}}$$

This precipitate contains barium and titanium in the correct ratio and is easily decomposed by heat, to give the oxide. The temperature used for this final heating is 920K.

$$\mathrm{Ba[TiO((COO)_2)_2]_{(s)}} \longrightarrow \mathrm{BaTiO_{3(s)} + 2CO_{2(g)} + 2CO_{(g)}}$$

The decomposition of oxalates is also used to prepare ferrites MFe2O4, which are important as magnetic materials. The products of the precursor method are usually crystalline solids, often containing small particles of large surface area. For some applications, such as catalysis and barium titanate capacitors, this is an advantage.

Coprecipitation-Synthesis of $ZnFe_2O_4$

Mix the oxalates of zinc and iron together in water in a 1:1 ratio. Heat to evaporate off the water. As the amount of H_2O decreases, a mixed Zn/Fe oxalate (probably hydrated) precipitates out.

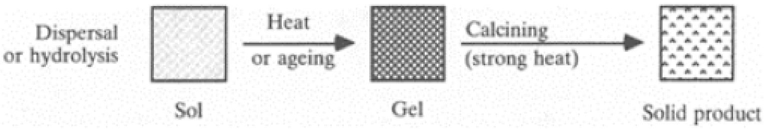
$$Fe_2((COO)_2)_3 + Zn(COO)_2 \longrightarrow Fe_2Zn((COO)_2)_5{*}xH_2O$$

After most of the water is gone, the precipitate is filtered and calcined at 1000 °C.

$$Fe_2Zn((COO)_2)_5 \longrightarrow ZnFe_2O_4 + 4CO + 4CO_2$$

The Sol-Gel Method

The precipitation methods always have the disadvantage that the stoichiometry of the precipitate(s) may not be exact if one or more ions are left in solution. The solgel method overcomes this because the reactants never precipitate out. First, a concentrated solution or colloidal suspension of the reactants, the ‘sol’, is prepared, which is then concentrated or matured to form the ‘gel’. This homogeneous gel is then heat-treated to form the product. The main steps in the sol-gel process are outlined in Figure.



The first investigation of a sol-gel process for synthesis was made in the mid-19th century. This early investigation studied the preparation of silica glass from a sol made by hydrolysing an alkoxide of silicon. Unfortunately, to prevent the product cracking and forming a fine powder, an aging period of a year or more was required! The sol-gel method was further developed in the 1950s and 1960s after it was realised that colloids, which contain small particles (1–1000 nm in diameter), could be highly chemically homogeneous.

A sol is a colloidal suspension of particles in a liquid; for the materials being discussed here, these particles will typically be 1 to 100 nm in diameter. A gel is a semi-rigid solid in which the solvent is contained in a framework of material which is either colloidal (essentially a concentrated sol) or polymeric.

To prepare solids using the sol-gel method, a sol of reactants is first prepared in a suitable liquid. Sol preparation can be either simply the dispersal of an insoluble solid or addition of a precursor which reacts with the solvent to form a colloidal product. A typical example of the first is the dispersal of oxides or hydroxides in water with the pH adjusted so that the solid particles remain in suspension rather than precipitate out. A typical example of the second method is the addition of metal alkoxides to water; the alkoxides are hydrolysed giving the oxide as a colloidal product.

The sol is either then treated or simply left to form a gel over time by dehydrating and/or polymerizing. To obtain the final product, the gel is heated. This heating serves several purposes—it removes the solvent, it decomposes anions such as alkoxides or carbonates to give oxides, it allows rearrangement of the structure of the solid, and it allows crystallisation to occur. Both the time and the temperature needed for reaction in sol-gel processes can reduced from those in the direct ceramic method; in favourable cases, the time from days to hours, and the temperature by several hundred degrees. Several examples discussed below illustrate the method; two of the examples have been chosen because they have interesting properties and uses, discussed later on in this book. Many other materials have been prepared by the sol-gel method, and other sol-gel preparations have been employed for the materials chosen. Therefore, these examples should be taken as illustrative and not as the main uses of the method.

Solid State Synthesis

Select appropriate starting materials

a) Fine grain powders to maximize surface area
b) Reactive starting reagents are better than inert
c) Well defined compositions

Weigh out starting materials, Mix starting materials together

a) Agate mortar and pestle (organic solvent optional)
b) Ball Mill (Especially for large preps > 20g)

Pelletize, Select sample container

Reactivity, strength, cost, ductility are all important
a) Ceramic refractories (crucibles and boats) Al_2O_3 1950°C $30/(20 ml) ZrO_2/Y_2O_3 2000 °C
b) Precious Metals (crucibles, boats and tubes) Pt 1770°C $500/(10 ml) Au 1063°C
c) Sealed Tubes SiO_2-Quartz, Au, Ag, Pt

Heat

a) Factors influencing choice of temperature for volatilization
b) Initial heating cycle to lower temperature can help to prevent spillage and volatilization
c) Atmosphere is also critical Oxides (Oxidizing Conditions) –Air, O_2, Low Temps
Oxides (Reducing Conditions) –H_2/Ar, CO/CO_2, High T Nitrides –NH_3or Inert (N_2, Ar, etc.)
Sulfides –H_2S Sealed tube reactions, Vacuum furnaces

Grind product and analyze (x-ray powder diffraction), If reaction incomplete, return to step 4 and repeat.

Example

1. Synthesis of Sr_2CrTaO_6

1) Possible starting reagents

Sr Metal –Hard to handle, prone to oxidation SrO-Picks up CO_2& water, mp = 2430°C $Sr(NO_3)_2$–mp = 570°C, may pick up some water $SrCO_3$–decomposes to SrO at 1370°C Ta Metal –mp = 2996°C Ta_2O_5–mp = 1800°C Cr Metal –Hard to handle, prone to oxidation
Cr_2O_3–mp = 2435°C $Cr(NO_3)_3*nH_2O$ –mp = 60°C, composition inaccurate To make 5.04 g of Sr_2CrTaO_6 (FW = 504.2 g/mol; 0.01 mol)

Complete the reaction:

$$4SrCO_3 + Ta_2O_5 + Cr_2O_3 \longrightarrow 2Sr_2CrTaO_6 + 4CO_2$$

Required Chemicals:

$SrCO_3$ 2.9526 g (0.02 mol)
Ta_2O_5 2.2095 g (0.005 mol)

Cr_2O^3 0.7600 g (0.005 mol)

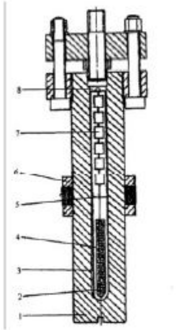
Applying Tamman'sruleto each of the reagents:

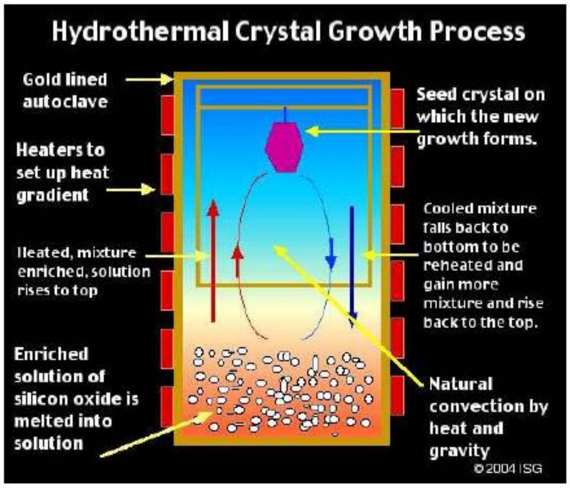
$SrCO_3$⇒SrO_{13} 70 °C (1643 K), SrO mp = 2700 K (mp = 1527 °C), Ta_2O_5 mp = 2070 K (mp = 1107 °C), Cr_2O_3mp = 2710 K (mp = 1532 °C)

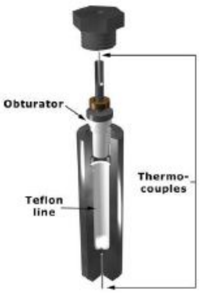
Although you may get a complete reaction by heating to 1150°C, in practice there will still be a fair amount of unreactedCr_2O_3. Therefore, to obtain a complete reaction it is best to heat to 1500-1600°C.

Hydrothermal synthesis

Uses a temperature gradient to dissolve the reactant at higher temperature, which is transported up the reaction tube by convection, then crystallizes out at a lower temperature.







Hydrothermal synthesis of CrO_2

Cr_2O_3 is the stable oxide of chromium at normal conditions.

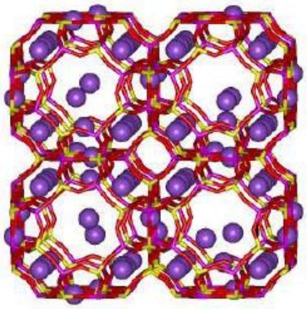
$Cr_2O_3 + CrO_3 \rightarrow 3CrO_2$

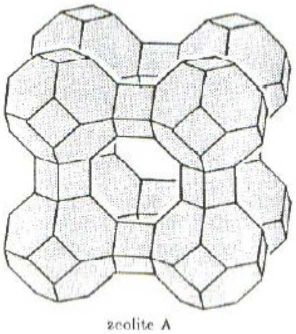
$CrO_3 \rightarrow CrO_2 + \frac{1}{2}O_2$

$3CrO_3 + Cr_2O_3 \rightarrow 5CrO_2 + O_2$

Hydrothermal synthesis of zeolite A, $Na_{12}[(AlO_2)_{12}\ (SiO_2)_{12}]$▪$27H_2O$.

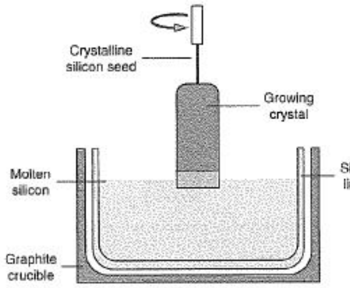
- Hydrated alumina, Al_2O_3▪$3H_2O$ is dissolved in concentrated NaOH.
- The cooled solution is mixed with sodium metasilicate, Na_2SiO_3▪$9H_2O$ and a thick white gel forms.
- The gel is placed in a closed teflon bottle and heated to 363 K over 6 hours.
- Changes in the form of alumina, pH of the solution, type of base used, and proportions of alkali, aluminum compound, and silica lead to the production of different zeolites.

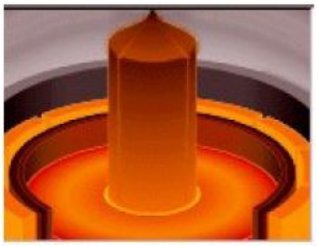




Czochralski Process

Silicon for the electronics industry has to have low levels of impurities, less than one impurity atom in 1010 Si. $SiHCl_3$ is highly volatile and distilled and decomposed as polycrystalline material onto rods of high purity silicon at 1300 K. Large single crystals are made by the Czochralski process. The silicon is melted in an atmosphere of Ar, then a single crystal seed rod is used as a seed which is dipped into the melt. The crystal is slowly withdrawn, pulling an ever lengthening single crystal in the same orientation as the original seed.





Preparing Single Crystals

Epitaxy methods:

Vapor Phase Epitaxy – possible to prepare high purity thin films. The epitaxial growth, a precursor is decomposed in the gas phase and a single crystal is built up layer by layer.

Gallium Arsenide (GaAs)

$2Ga_{(g)}+ 2AsCl_{3(g)} \rightarrow 2GaAs_{(s)} + 3Cl_{2(g)}$

or

$Ga(CH_3)_{3(g)} + AsH_{3(g)} \rightarrow GaAs + 3CH4_{(g)}$

Mercury Telluride (HgTe)

$(C_2H_5)_2Te_{(g)}+ Hg_{(g)} \text{ ----}H_2\text{, UV light}\rightarrow HgTe_{(s)}$

Substrate temperature = 470 K, about 200 °C lower than thermal decomposition temperature.

Intercalation

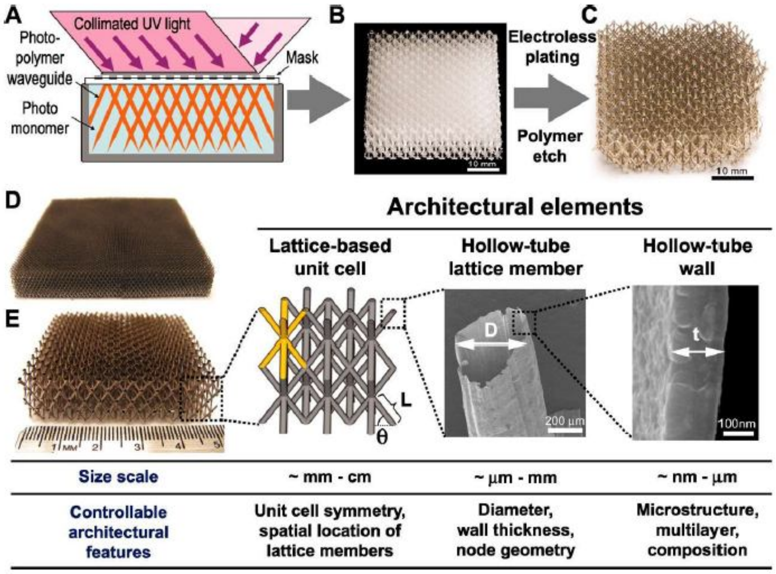
Solids produced by the reversible insertion of guest molecules into lattices are known as intercalation compounds.

Graphite intercalation compounds

- Many layered solids form intercalation compounds, where a neutral molecule is inserted between weakly bonded layers.
- KC8 has potassium ions that sit between the graphite layers, with a resulting increase in the interlayer spacing of 200 pm.
- The K donates an electron to the graphite (forming K+) and the conductivity of the graphite increases.
- Graphite electron-acceptor intercalation compounds have been made with NO3 -, CrO_3, Br_2, $FeCl_3$, AsF_5.

Titanium Disulfide

- Layered sulfide are also found for many oxides and sulfides of transition metals.
- Forming intercalation compounds with electron donors can greatly increase the conductivity.
- $xC_4H_9Li + TiS_2 \rightarrow Li_xTiS_2 + (x/2)C_8H_{18}$



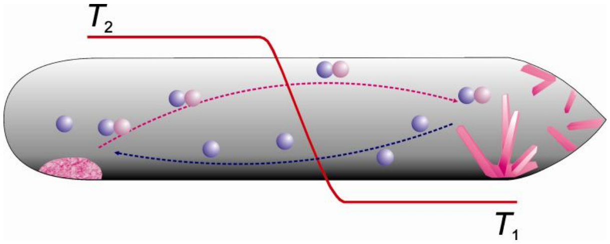
Ion exchange

Many solid state materials can be ion exchanged under moderate conditions. Zeolites and α zirconium phosphates can be ion exchanged in water. β aluminas and $NaZr_2(PO_4)_3$ type materials can be ion exchanged in molten salts.

$$NaAl_{11}O_{17} + AgNO_3\ (300^{o}C) \dashrightarrow AgAl_{11}O_{17} + NaNO_3$$

CHEMICAL VAPOR TRANSPORT REACTIONS

A variety of processes of crystal growth proceeds via the gas phase. A short comparative overview on gas phase transports is given here. However, in the main we deal with the concept of Chemical Vapor Transport Reactions. The term “Chemical Vapor Transport” (CVT) summarizes heterogeneous reactions which show one shared feature: a condensed phase, typically a solid, has an insufficient pressure for its own volatilization. But the pertinent phase can be volatilized in the presence of a gaseous reactant, the transport agent, and deposits elsewhere, usually in the form of crystals. The deposition will take place if there are different external conditions for the chemical equilibrium at the position of crystallization than at the position of volatilization. Usually, different temperatures are applied for volatilization and crystallization,



Chemical vapor transport reactions address the formation process of pure and crystalline solids. Especially, the growth of single-crystalline material is of particular value because, among other things, it allows the determination of the crystal structure by diffraction methods. Beyond the aspect of basic research, chemical vapor transport reactions have also gained practical significance: they form the basis of the operating mode of halogen lamps. Furthermore, an industrial process is based on a chemical transport reaction, the Mond-Langer-Process for the production of ultrapure nickel. Chemical vapor transports likewise occur in nature forming minerals without human influence, in particular at places of high temperatures. Bunsen was the first who observed and described it. He noticed that the formation of crystalline Fe_2O_3 is associated with the presence of volcanic gases which contain gaseous hydrogen chloride. Van Arkel and de Boer were the first scientists who carried out specific transport reactions in the laboratory from 1925 onwards. They were motivated by the huge interest in finding a process to fabricate pure metals like titanium at that time. Van Arkel and de Boer used the so called glowing wire method. In the process, the contaminated metal M (e.g. a metal of the 4th group) transforms into a gaseous metal iodide (MIn) in the presence of iodine as the transport agent. The iodide is formed at the metal surface in an exothermic reaction and vaporizes completely, thus reaching a glowing wire which was heated up to high temperatures. On the glowing wires surface, the back reaction (that is the endothermic reaction) is favored by Le Chatelier's principle. That way the decomposition of the metal iodide via the metals deposition proceeds and the metal is deposited on the hot wire.

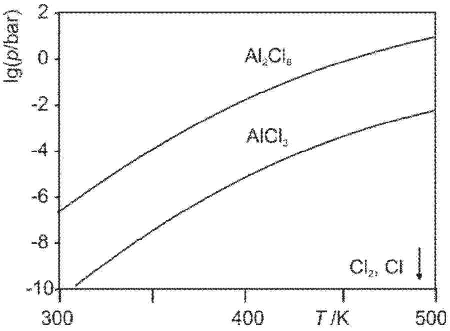
OVERVIEW ON VAPOR TRANSPORT METHODS

A vast number of reactions involving gas phases hardly differ from each other: If a condensed substance encounters a temperature gradient, it moves from the place of dissolution via the gas phase to the place of deposition, from **source** to **sink**. However, we do not "see" how the substance is led to the gas phase and deposited at another place. The mechanisms of gas phase transports can be deduced from experimental determination of the gas phase composition and/or from thermodynamic considerations of the pertinent heterogeneous equilibria between the solid and the gas phase.

Sublimation: Sublimations occurs without decomposition of the initial solid by forming only one dominating gas species. Substances showing sublimation are often solids constituting of molecular units, which are "bonded" by only weak interactions. The much stronger (covalent) bond in the molecular unit persist even under external energy stress, and the molecule can sublime undecomposed. Iodine, I_2 is a concise example of sublimation.

I2(s)⇄I2(g)

The other possible gas species in the system, I(g) is of less importance due to the significantly lower partial pressures at the temperature of sublimation.



Saline solids can sublime, too. A well-known example is aluminum(III) chloride which is present in the gas phase in large proportion in form of dimeric molecule Al_2Cl_6. The additional systems gas species, such as $AlCl_3$(g), Cl_2(g), and Cl(g) show significantly lower partial pressures at the given temperature and thus not take part in the evaporation process.

2 AlCl3(s)⇄Al2Cl6(g)

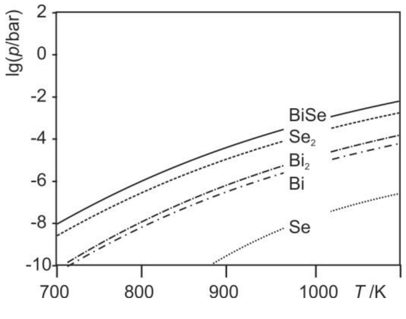
In a generalized form, the sublimation of a compound AB_x is described by equilibrium.

ABx(s) ⇄ABx(g)

Decomposition sublimation: If there is no stable molecular unit which is evaporable, a solid can decompose into various gaseous products while heating. Changing the equilibrium conditions, the initial solid can be recovered out of such a gas phase. This is called decomposition sublimation.

The gas phase transport of bimuth(III) selenide - Bi_2Se_3, an important constituent for thermoelectric materials - shows the characteristic of that. It decomposes into stoichiometric amounts of BiSe(g) and Se_2(g) in the vapor phase, the molecule of the initial composition Bi_2Se_3(g) does not occur in evaporation process. During cooling, the gas phase condenses completely and solid solid bimuth(III) selenide is formed.

Bi2Se3(s)⇄2BiSe(g)+1/2 Se2(g)



Hydrothermal synthesis

Hydrothermal synthesis includes the various techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures; also termed "hydrothermal method". The term "hydrothermal" is of geologic origin. Geochemists and mineralogists have studied hydrothermal phase equilibria since the beginning of the twentieth century. George

W. Morey at the Carnegie Institution and later, Percy W. Bridgman at Harvard University did much of the work to lay the foundations necessary to containment of reactive media in the temperature and pressure range where most of the hydrothermal work is conducted.

Hydrothermal synthesis can be defined as a method of synthesis of single crystals that depends on the solubility of minerals in hot water under high pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called an autoclave, in which a nutrient is supplied along with water. A temperature gradient is maintained between the opposite ends of the growth chamber. At the hotter end the nutrient solute dissolves, while at the cooler end it is deposited on a seed crystal, growing the desired crystal.

Advantages of the hydrothermal method over other types of crystal growth include the ability to create crystalline phases which are not stable at the melting point. Also, materials which have a high vapour pressure near their melting points can be grown by the hydrothermal method. The method is also particularly suitable for the growth of large good-quality crystals while maintaining control over their composition. Disadvantages of the method include the need of expensive autoclaves, and the impossibility of observing the crystal as it grows.

Equipment for hydrothermal crystal growth

The crystallization vessels used are autoclaves. These are usually thick-walled steel cylinders with a hermetic seal which must withstand high temperatures and pressures for prolonged periods of time. Furthermore, the autoclave material must be inert with respect to the solvent. The closure is the most important element of the autoclave. Many designs have been developed for seals, the most famous being the Bridgman seal. In most cases, steel-corroding solutions are used in hydrothermal experiments. To prevent corrosion of the internal cavity of the autoclave, protective inserts are generally used. These may have the same shape as the autoclave and fit in the internal cavity (contact-type insert), or be a "floating" type insert which occupies only part of the autoclave interior. Inserts may be made of carbon-free iron, copper, silver, gold, platinum, titanium, glass (or quartz), or Teflon, depending on the temperature and solution used.

Methods

Temperature-difference method

This is the most extensively used method in hydrothermal synthesis and crystal growing. Supersaturation is achieved by reducing the temperature in the crystal growth zone. The nutrient is placed in the lower part of the autoclave filled with a specific amount of solvent. The autoclave is heated in order to create two temperature zones. The nutrient dissolves in the hotter zone and the saturated aqueous solution in the lower part is transported to the upper part by convective motion of the solution. The cooler and denser solution in the upper part of the autoclave descends while the counterflow of solution ascends. The solution becomes supersaturated in the upper part as the result of the reduction in temperature and crystallization sets in.

Temperature-reduction technique

In this technique crystallization takes place without a temperature gradient between the growth and dissolution zones. The supersaturation is achieved by a gradual reduction in temperature of the solution in the autoclave. The disadvantage of this technique is the difficulty in controlling the growth process and introducing seed crystals. For these reasons, this technique is very seldom used.

Metastable-phase technique

This technique is based on the difference in solubility between the phase to be grown and that serving as the starting material. The nutrient consists of compounds that are thermodynamically unstable under the growth conditions. The solubility of the metastable phase exceeds that of the stable phase, and the latter crystallize due to the dissolution of the metastable phase. This technique is usually combined with one of the other two techniques above.

High Pressure Method

Pascalization, bridgmanization, high pressure processing (HPP) or high hydrostatic pressure (HHP) processing is a method of preserving and sterilizing food, in which a product is processed under very high pressure, leading to the inactivation of certain microorganisms and enzymes in the food. The technique was named after Blaise Pascal, a French scientist of the 17th century whose work included detailing the effects of pressure on fluids. During pascalization, more than 50,000 pounds per square inch (340 MPa, 3.4 kbar) may be applied for around fifteen minutes, leading to the inactivation of yeast, mold, and bacteria. Pascalization is also known as bridgmanization, named for physicistPercy Williams Bridgman.

Process

In pascalization, food products are sealed and placed into a steel compartment containing a liquid, often water, and pumps are used to create pressure. The pumps may apply pressure constantly or intermittently.[1] The application of high hydrostatic pressures (HHP) on a food product will kill many microorganisms, but the spores of some bacteria may need to be separately treated with acid to prevent their reproduction. Pascalization works especially well on acidic foods, such as yogurts and fruits, because pressure-tolerant spores are not able to live in environments with low pH levels. The treatment works equally well for both solid and liquid products.

During pascalization, the food's proteins are denatured, hydrogen bonds are fortified, and noncovalent bonds in the food are disrupted, while the product's main structure remains intact. Because pascalization is not heat-based, covalent bonds are not affected, causing no change in the food's taste. High hydrostatic pressure can affect muscle tissues by increasing the rate of lipid oxidation, which in turn leads to poor flavor and decreased health benefits.
Because hydrostatic pressure is able to act quickly and evenly on food, neither the size of a product's container nor its thickness play a role in the effectiveness of pascalization. There are several side effects of the process, including a slight increase in a product's sweetness, but pascalization does not greatly affect the nutritional value, taste, texture, and appearance. As a result, high pressure treatment of foods is regarded as a "natural" preservation method, as it does not use chemical preservatives.

Zone melting

Zone melting (or zone refining or floating zone process or travelling melting zone) is a group of similar methods of purifying crystals, in which a narrow region of a crystal is melted, and this molten zone is moved along the crystal. The molten region melts impure solid at its forward edge and leaves a wake of purer material solidified behind it as it moves through the ingot. The impurities concentrate in the melt, and are moved to one end of the ingot. Zone refining was invented by John Desmond Bernal and further developed by William Gardner Pfann in Bell Labs as a method to prepare high purity materials, mainly semiconductors, for manufacturing transistors. Its early use was on germanium for this purpose, but it can be extended to virtually any solute-solvent system having an appreciable concentration difference between solid and liquid phases at equilibrium.[2] This process is also known as the float zone process, particularly in semiconductor materials processing.

Process details

The principle is that the segregation coefficient k (the ratio of an impurity in the solid phase to that in the liquid phase) is usually less than one. Therefore, at the solid/liquid boundary, the impurity atoms will diffuse to the liquid region. Thus, by passing a crystal boule through a thin section of furnace very slowly, such that only a small region of the boule is molten at any time, the impurities will be segregated at the end of the crystal. Because of the lack of impurities in the leftover regions which solidify, the boule can grow as a perfect single crystal if a seed crystal is placed at the base to initiate a chosen direction of crystal growth. When high purity is required, such as in semiconductor industry, the impure end of the boule is cut off, and the refining is repeated.

In zone refining, solutes are segregated at one end of the ingot in order to purify the remainder, or to concentrate the impurities. In zone leveling, the objective is to distribute solute evenly throughout the purified material, which may be sought in the form of a single crystal. For example, in the preparation of a transistor or diode semiconductor, an ingot of germanium is first purified by zone refining. Then a small amount of antimony is placed in the molten zone, which is passed through the pure germanium. With the proper choice of rate of heating and other variables, the antimony can be spread evenly through the germanium. This technique is also used for the preparation of silicon for use in computer chips.

Zone remelting

Another related process is zone remelting, in which two solutes are distributed through a pure metal. This is important in the manufacture of semiconductors, where two solutes of opposite conductivity type are used. For example, in germanium, pentavalent elements of group Vsuch as antimony and arsenic produce negative (n-type) conduction and the trivalent elements of group III such as aluminum and boronproduce positive (p-type) conduction. By melting a portion of such an ingot and slowly refreezing it, solutes in the molten region become distributed to form the desired n-p and p-n junctions.

Czochralski process

The Czochralski process is a method of crystal growth used to obtain single crystals of semiconductors (e.g. silicon, germanium and gallium arsenide), metals (e.g. palladium, platinum, silver, gold), salts and synthetic gemstones. The process is named after Polish scientist Jan Czochralski, who invented the method in 1915 while investigating the crystallization rates of metals. He made this discovery by accident, while studying the crystallization rate of metals when, instead of dipping his pen into the ink, he did so in molten tin and drew a tinfilament, that later proved to be a single crystal.

The most important application may be the growth of large cylindrical ingots, or boules, of single crystal silicon used in the electronics industry to make semiconductor devices like integrated circuits. Other semiconductors, such as gallium arsenide, can also be grown by this method, although lower defect densities in this case can be obtained using variants of the Bridgman-Stockbarger technique.

Crystal sizes

Due to the efficiencies of common wafer specifications, the semiconductor industry has used wafers with standardized dimensions. In the early days, the boules were smaller, only a few inches wide. With advanced technology, high-end device manufacturers use 200 mm and 300 mm diameter wafers. The width is controlled by precise control of the temperature, the speeds of rotation and the speed the seed holder is withdrawn. The crystal ingots from which these wafers are sliced can be up to 2 metres in length, weighing several hundred kilograms. Larger wafers allow improvements in manufacturing efficiency, as more chips can be fabricated on each wafer, so there has been a steady drive to increase silicon wafer sizes. The next step up, 450 mm, is currently scheduled for introduction in 2018. Silicon wafers are typically about 0.2–0.75 mm thick, and can be polished to great flatness for making integrated circuits or textured for making solar cells.

The process begins when the chamber is heated to approximately 1500 degrees Celsius, melting the silicon. When the silicon is fully melted, a small seed crystal mounted on the end of a rotating shaft is slowly lowered until it just dips below the surface of the molten silicon. The shaft rotates counter clockwise and the crucible rotates clockwise. The rotating rod is then drawn upwards very slowly about 25 mm per hour when making a crystal of ruby allowing a roughly cylindrical boule to be formed. The boule can be from one to two metres, depending on the amount of silicon in the crucible. The electrical characteristics of the silicon are controlled by adding material like phosphorus or boron to the silicon before it is melted. The added material is called dopant and the process is called doping. This method is also used with semiconductor materials other than silicon, such as gallium arsenide.

Application

Monocrystalline silicon (mono-Si) grown by the Czochralski process is often referred to as monocrystalline Czochralski silicon (Cz-Si). It is the basic material in the production of integrated circuits used in computers, TVs, mobile phones and all types of electronic equipment and semiconductor devices. Monocrystalline silicon is also used in large quantities by the photovoltaic industry for the production of conventional mono-Si solar cells. The almost perfect crystal structure yields the highest light-to-electricity conversion efficiency for silicon.

Bridgman–Stockbarger technique

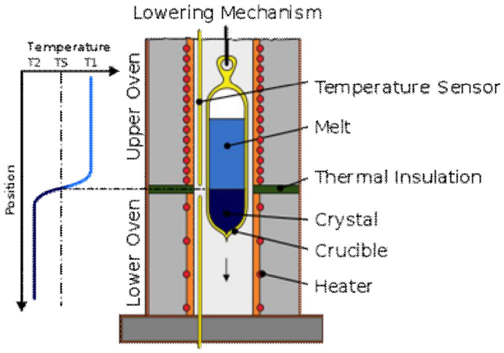
The Bridgman–Stockbarger technique is named after Harvard physicist Percy Williams Bridgman (1882-1961) and MIT physicist Donald C. Stockbarger (1895–1952). The technique includes two similar but distinct methods primarily used for growing boules (single crystal ingots), but which can be used for solidifying polycrystalline ingots as well.

The methods involve heating polycrystalline material above its melting point and slowly cooling it from one end of its container, where a seed crystal is located. A single crystal of the same crystallographic orientation as the seed material is grown on the seed and is progressively formed along the length of the container. The process can be carried out in a horizontal or vertical orientation, and usually involves a rotating crucible/ampoule to stir the melt.

The Bridgman method is a popular way of producing certain semiconductor crystals such as gallium arsenide, for which the Czochralski process is more difficult. The process can reliably produce single crystal ingots, but does not necessarily result in uniform properties through The difference between the Bridgman technique and Stockbarger[3] technique is subtle: While both methods utilize a temperature gradient and a moving crucible, the Bridgman technique utilizes the relatively uncontrolled gradient produced at the exit of the furnace; the Stockbarger technique introduces a baffle, or shelf, separating two coupled furnaces with temperatures above and below the freezing point. Stockbarger's modification of the Bridgman technique allows for better control over the temperature gradient at the melt/crystal interface.

When seed crystals are not employed as described above, polycrystalline ingots can be produced from a feedstock consisting of rods, chunks, or any irregularly shaped pieces once they are melted and allowed to re-solidify. The resultant microstructures of the ingots so obtained are characteristic of directionally solidified metals and alloys with their aligned grains.

A variant of the technique known as the horizontal directional solidification method or HDSM developed by Khachik Bagdasarov starting in the 1960s in the Soviet Union uses a flat-bottomed crucible with short sidewalls rather than an enclosed ampoule, and has been used to grow various large oxide crystals including Yb:YAG (a laser host crystal) and sapphire crystals 45 cm wide and over 1 meter long.



Single crystal

A single crystal or monocrystalline solid is a material in which the crystal lattice of the entire sample is continuous and unbroken to the edges of the sample, with no grain boundaries. The absence of the defects associated with grain boundaries can give monocrystals unique properties, particularly mechanical, optical and electrical, which can also be anisotropic, depending on the type of crystallographic structure. These properties, in addition to making them precious in some gems, are industrially used in technological applications, especially in optics and electronics.

Because entropic effects favour the presence of some imperfections in the microstructure of solids, such as impurities, inhomogeneous strain and crystallographic defects such as dislocations, perfect single crystals of meaningful size are exceedingly rare in nature, and are also difficult to produce in the laboratory, though they can be made under controlled conditions. On the other hand, imperfect single crystals can reach enormous sizes in nature: several mineral species such as beryl, gypsum and feldspars are known to have produced crystals several metres across. The opposite of a single crystal is an amorphous structure where the atomic position is limited to short range order only. In between the two extremes exist polycrystalline, which is made up of a number of smaller crystals known as crystallites, and paracrystalline phases.

Uses

Semiconductor industry

Single crystal silicon is used in the fabrication of semiconductors. On the quantum scale that microprocessors operate on, the presence of grain boundaries would have a significant impact on the functionality of field effect transistors by altering local electrical properties. Therefore, microprocessor fabricators have invested heavily in facilities to produce large single crystals of silicon.

Optics

- Monocrystals of sapphire and other materials are used for lasers and nonlinear optics.
- Monocrystals of fluorite are sometimes used in the objective lenses of apochromatic refracting telescopes.

Materials engineering

Another application of single crystal solids is in materials science in the production of high strength materials with low thermal creep, such as turbine blades.[1][2] Here, the absence of grain boundaries actually gives a decrease in yield strength, but more importantly decreases the amount of creep which is critical for high temperature, close tolerance part applications.

Electrical conductors

Single crystals provide a means to understand, and perhaps realize, the ultimate performance of metallic conductors. Of all the metallic elements, silver and copper have the best conductivity at room temperature, so set the bar for performance. The size of the market, and vagaries in supply and cost, have provided strong incentives to seek alternatives or find ways to use less of them by improving performance.

The conductivity of commercial conductors is often expressed relative to the International Annealed Copper Standard, according to which the purest copper wire available in 1914 measured around 100%. The purest modern copper wire is a better conductor, measuring over 103% on this scale. The gains are from two sources. First, modern copper is more pure. However, this avenue for improvement seems at an end. Making the copper purer still makes no significant improvement. Second, annealing and other processes have been improved. Annealing reduces the dislocations and other crystal defects which are sources of resistance. But the resulting wires are still polycrystalline. The grain boundaries and remaining crystal defects are responsible for some residual resistance. This can be quantified and better understood by examining single crystals. As anticipated, single-crystal copper did prove to have better conductivity than polycrystalline copper.

But there were surprises in store (see table). The single-crystal copper not only became a better conductor than high purity polycrystalline silver, but with prescribed heat and pressure treatment could surpass even single-crystal silver. And although impurities are usually bad for conductivity, a silver single-crystal with a small amount of copper substitutions was a better conductor than them all. As of 2009, no single-crystal copper is manufactured on a large scale industrially, but methods of producing very large individual crystal sizes for copper conductors are exploited for high performance electrical applications. These can be considered meta-single crystals with only a few crystals per metre of length.

In research

Single crystals are essential in research especially condensed-matter physics, materials science, surface scienceetc. The detailed study of the crystal structure of a material by techniques such as Bragg diffraction and helium atom scattering is much easier with monocrystals. Only in single crystals it is possible to study directional dependence of various properties. Furthermore, techniques such as scanning tunneling microscopy are only possible on surfaces of single crystals. In superconductivity there have been cases of materials where superconductivity is only seen in single crystalline specimen. They may be grown for this purpose, even when the material is otherwise only needed in polycrystalline form.

Manufacture

In the case of silicon and metal single crystal fabrication the techniques used involve highly controlled and therefore relatively slow crystallization. Specific techniques to produce large single crystals (aka boules) include the Czochralski process and the Bridgman technique. Other less exotic methods of crystallization may be used, depending on the physical properties of the substance, including hydrothermal synthesis, sublimation, or simply solvent-based crystallization.

A different technology to create single crystalline materials is called epitaxy. As of 2009, this process is used to deposit very thin (micrometre to nanometer scale) layers of the same or different materials on the surface of an existing single crystal. Applications of this technique lie in the areas of semiconductor production, with potential uses in other nanotechnological fields and catalysis.

Single Crystal Growth

A single crystal, also called monocrystal, is a crystalline solid in which the crystal lattice of the entire sample is continuous and unbroken to the edges of the sample, with no grain boundaries. Grain boundaries have a lot of significant effects on the mechanical, physical and electrical properties of materials. Therefore, single crystals are demanded in many fields, such as microelectronics and optoelectronics, as well as structural and high temperature materials.

Flame fusion: The raw materials are added to the top chamber of the furnace. Oxygen and hydrogen are blown into the cabin for combustion, where a high temperature is achieved. Liquid droplets of materials form single crystal at the tip. This method could provide a high growing speed. The quality of the crystal produced, however, is limited by the irregular temperature distribution and cooling velocity.

Czochralski: In the Czochralski method, a single crystal is pulled from the melt. This method has had nearly one hundred years' history, whereas currently is still the most widely used method to fabricate single crystal materials, especially large semiconductor and metallic materials. It can produce very high quality crystals.

Bridgman-Stockbarger: In this method, the central chamber is turning as well as pushed down, from the high temperature region towards the low temperature region. The solid liquid interface is moved along the charge.

Floating Zone: Floating zone crystal growth is a method developed from Bridgman-Stockbarger method. It is most broadly utilized in growing cylindrical boules of very high purity Silicon single crystal. Its main advantage is the absence of crucible which is one of the sources of contamination in the other methods. It is arguably one of the most enabling techniques developed in the information era, to allow integrated circuits to be mass produced on smaller scales.

Solution growth: The basic idea of this method is to achieve an over-saturated solution first and then to have it crystallized. It is particularly adapted to non congruent materials and/or very high melting point compounds. The limitation of this method lies in the choice of appropriate solvent. For each particular crystal that is demanded, there should be some certain solvent, either water, or molten salt or metals, to provide a stable crystallization.

Hydrothermal: Hydrothermal synthesis can be defined as a method of synthesis of single crystals which depends on the solubility of minerals in hot water under high pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called autoclave, in which a nutrient is supplied along with water. A gradient of temperature is maintained at the opposite ends of the growth chamber so that the hotter end dissolves the nutrient and the cooler end causes seeds to take additional growth.

Sublimation: When materials cannot be grown from the liquid phase, the sublimation method could be a good alternative. It uses solid in a powder state as a source. Generally the crystal quality is more difficult to control than when the growth is done from the liquid phase. Applications:

Applications of single crystal materials are broad.

Silicon single crystals and related materials have a large market in integrated circuits industry. Monocrystals of sapphire are highly demanded in laser devices. For metallic materials, turbine blades can be made of single crystals of superalloys, which can achieve novel mechanical properties.

Electrochemical reduction of carbon dioxide

The electrochemical reduction of carbon dioxide (ERC) is the conversion of carbon dioxide to more reduced chemical species using electrical energy. The first examples of electrochemical reduction of carbon dioxide are from the 19th century, when carbon dioxide was reduced to carbon monoxide using a zinc cathode. Research in this field intensified in the 1980s following the oil embargoes of the 1970s. Electrochemical reduction of carbon dioxide represents a possible means of producing chemicals or fuels, converting carbon dioxide (CO_2) to organic feedstocks such as formic acid (HCOOH), methanol (CH_3OH), ethylene (C_2H_4), methane (CH_4), and carbon monoxide (CO).

Chemicals from carbon dioxide

In carbon fixation, plants convert carbon dioxide into sugars, from which many biosynthetic pathways originate. The catalyst responsible for this conversion, RuBisCo, is the most common protein on earth. Some anaerobic organisms employ enzymes to convert CO_2 to carbon monoxide, from which fatty acids can be made. In industry, a few products are made from CO_2, including urea, salicylic acid, methanol, and certain inorganic and organic carbonates. In the laboratory, carbon dioxide is sometimes used to prepare carboxylic acids. No electrochemical process involving CO_2 has been commercialized.

Electrocatalysis

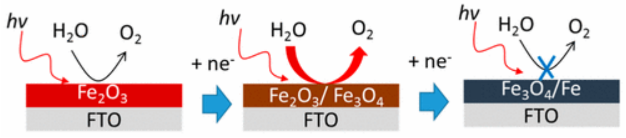
The electrochemical reduction of carbon dioxide to CO is usually described as:

$$CO_2 + 2\ H^+ + 2\ e^- \rightarrow CO + H_2O$$

The redox potential for this reaction is similar to that for hydrogen evolution in aqueous electrolytes, thus electrochemical reduction of CO2 is usually competitive with hydrogen evolution reaction. Electrochemical methods have gained significant attention: 1) at ambient pressure and room temperature; 2) in connection with renewable energy sources (see also solar fuel) 3) competitive controllability, modularity and scale-up is relatively simple. The electrochemical reduction or electrocatalytic conversion of CO_2 can produce value-added chemicals such methane, ethylene, ethane, etc., and the products are mainly dependent on the selected catalysts and operating potentials (applying reduction voltage).

Although an electrochemical route to CO (or other chemicals) has not been commercialized, a variety of homogeneous and heterogeneous catalysts have been evaluated. Many such processes are assumed to operate via the intermediacy of metal carbon dioxide complexes. Generally speaking, the processes developed up to 2010 either had poor thermodynamic efficiency (high overpotential), low current efficiency, low selectivity, slow kinetics, and/or poor stability. In 2011, workers from Dioxide Materials and University of Illinois showed that the combination of two catalysts could eliminate the high overpotential More recently, the same group showed that the process was stable for 6 months at over 90% selectivity.

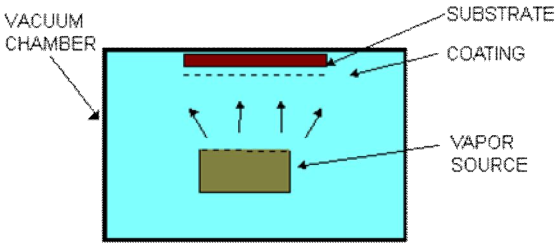
Electrochemical reduction method is used for the first time to significantly improve the photo-electrochemical performance of α-Fe_2O_3 photoanode prepared on fluorine-doped tin oxide substrates by spin-coating aqueous solution of $Fe(NO_3)_3$ followed by thermal annealing in air. Photocurrent density of α-Fe_2O_3 thin film photoanode can be enhanced 25 times by partially reducing the oxide film to form more conductive Fe_3O_4 (magnetite). Fe_3O_4 helps facilitate efficient charge transport and collection from the top α-Fe_2O_3 layer upon light absorption and charge separation to yield enhanced photocurrent density. The optimal enhancement can be obtained for <50 nm films because of the short charge transport distance for the α-Fe_2O_3 layer. Thick α-Fe_2O_3films require more charge and overpotential than thinner films to achieve limited enhancement because of the sluggish charge transport over a longer distance to oxidize water. Electrochemical reduction of α-Fe_2O_3 in unbuffered pH-neutral solution yields much higher but unstable photocurrent enhancement because of the increase in local pH value accompanied by proton reduction at a hematite surface.



Thin film preparation techniques

Film synthesis techniques used in the laboratory are based in physical or chemical vapor deposition of thin films ('physical vapour deposition' or PVD and 'chemical vapour deposition' or CVD, respectively). In both cases, the techniques are based in the formation of vapor of the material to be deposited, so that the vapor is condensed on the substrate surface as a thin film. Usually the process must be performed in vacuum or in controlled atmosphere, to avoid interaction between vapor and air.

Process diagram



- In physical techniques (PVD) we part from a solid material converted to vapor through heating (evaporation) or energetic ion bombardment. The material in form of vapor finally condeses on the substrate surface as a thin film.
- In chemical techniques (CVD) we part directly from gases (sometimes vapor originating from a liquid phase) which react and give place to a new product that condenses as a thin film on the substrate.
- Other film synthesis techniques include high temperature thermal oxidation and anodic oxidation.

An essential difference between PVD and CVD techniques is that in the first ones the material to be deposited already exists (in solid form), while in the second ones the material does not exist previously: it is synthesized in vapor phase.