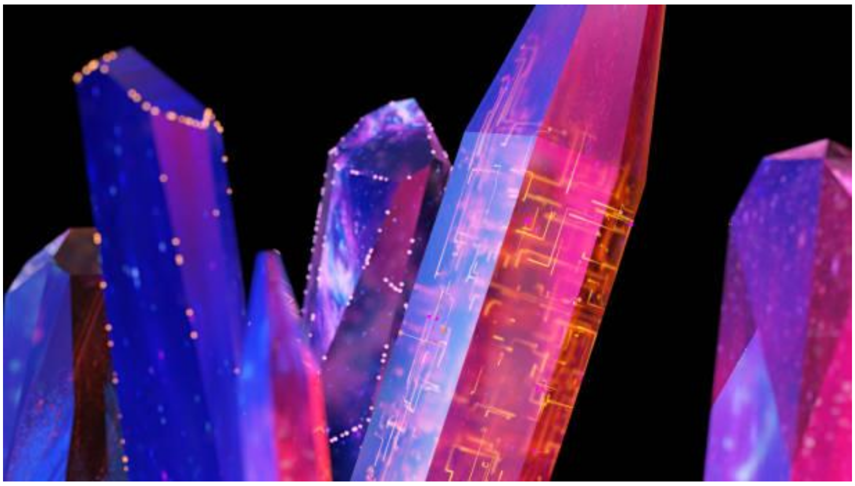
SOUTH VALLEY UNIVERSITY
جامعة جنوب الوادي

CRYSTAL GROWTH



BY

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Crystallization

Crystallization is the (natural or artificial) process of formation of solid crystals precipitating from a solution, melt or more rarely deposited directly from a gas. Crystallization is also a chemical solid-liquid separation technique, in which mass transfer of a solute from the liquid solution to a pure solid crystalline phase occurs.

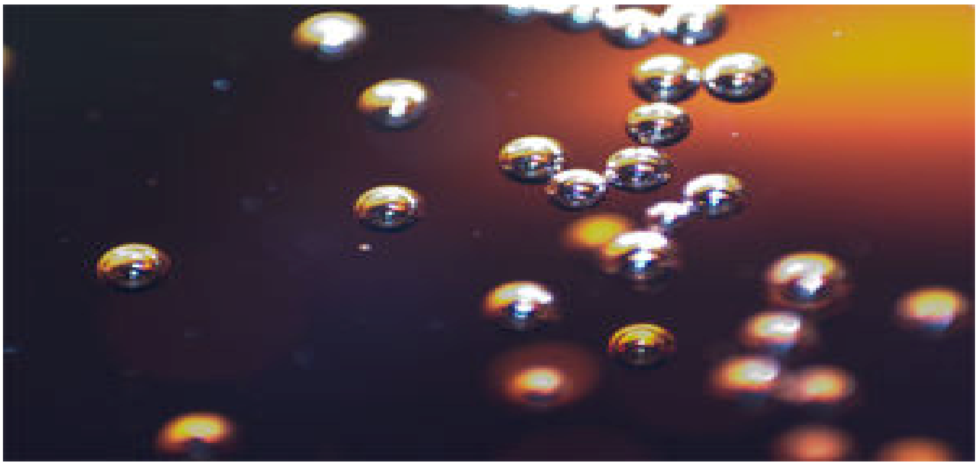
Process

The crystallization process consists of two major events, *nucleation* and *crystal growth*.

1- Nucleation

Nucleation is the onset of a phase transition in a small region. The phase transition can be the formation of a bubble or of a crystal from a liquid. Creation of liquid droplets in saturated vapor or the creation of gaseous bubble in a saturated liquid is also characterized by nucleation (see Cloud condensation nuclei). Nucleation of crystalline, amorphous, and even vacancy clusters in solid materials is also important, for example to the semiconductor industry.

Nucleation normally occurs at *nucleation sites* on surfaces containing the liquid or vapor. Suspended particles or minute bubbles also provide nucleation sites. This is called *heterogeneous nucleation*. Nucleation without preferential nucleation sites is *homogeneous nucleation*. Homogeneous nucleation occurs spontaneously and randomly, but it requires superheating or supercooling of the medium. Nucleation is involved in such processes as cloud seeding and in instruments such as the bubble chamber and the cloud chamber.



Examples of nucleation

- Nucleation of carbon dioxide bubbles around a finger
- Pure water freezes at −42° C rather than at its freezing temperature of 0° C if no crystal nuclei, such as dust particles, are present to form an ice nucleus.
- Presence of cloud condensation nuclei is important in meteorology because they are often in short supply in the upper atmosphere (*see cloud seeding*).
- All natural and artificial crystallization process (of formation of solid crystals from a homogeneous solution) starts with a *nucleation* event.
- Bubbles of carbon dioxide *nucleate* shortly after the pressure is released from a container of carbonated liquid. Nucleation often occurs more easily at a pre-existing interface (*heterogeneous*

nucleation), as happens on boiling chips and string used to make rock candy. So-called Diet Coke and Mentos eruptions are a dramatic example.

- Nucleation in boiling can occur in the bulk liquid if the pressure is reduced so that the liquid becomes superheated with respect to the pressure-dependent boiling point. More often nucleation occurs on the heating surface, at *nucleation sites*. Typically, nucleation sites are tiny crevices where free gas-liquid surface is maintained or spots on the heating surface with lower wetting properties. Substantial superheating of a liquid can be achieved after the liquid is de-gassed and if the heating surfaces are clean, smooth and made of materials well wetted by the liquid.
- Nucleation is a key concept in polymer, alloy, and ceramic systems.
- In chemistry and biophysics, nucleation can also refer to the phaseless formation of multimers which are intermediates in polymerization processes. This sort of process is believed to be the best model for processes such as crystallization and amyloidogenesis.

- In molecular biology, nucleation is used to term the critical stage in the assembly of a polymeric structure, such as a microtubule, at which a small cluster of monomers aggregates in the correct arrangement to initiate rapid polymerization. For instance, two actin molecules bind weakly, but addition of a third stabilizes the complex. This trimer then adds additional molecules and forms a nucleation site. The nucleation site serves the slow, or lag phase of the polymerization process.

Mechanics of nucleation

Homogeneous nucleation

Nucleation generally occurs with much more difficulty in the interior of a uniform substance, by a process called *homogeneous nucleation*. Liquids cooled below the maximum heterogeneous nucleation temperature (melting temperature), but which are above the homogeneous nucleation temperature (pure substance freezing temperature) are said to be supercooled. This is useful for making amorphous solids and other metastable structures, but can delay the progress of industrial chemical processes or produce undesirable effects in the context of casting.

The creation of a nucleus implies the formation of an interface at the boundaries of the new phase. Some energy is consumed to form this interface, based on the surface energy of each phase. If a hypothetical nucleus is too small, the energy that would be released by forming its volume is not enough to create its surface, and nucleation does not proceed. The critical nucleus size can be denoted by its radius, and it is when r=r* (or r critical) that the nucleation proceeds.

For example in the classic case of a spherical cluster that liberates $-G_v$ Joules per cubic centimeter during formation (here G_v is a negative quantity), but which must pay the positive cost of σ Joules per square centimeter of surface interfacing with the world around, the free energy needed to form a cluster of radius r is :

$$W = \frac{4}{3}\pi\ r^3\ G_v + 4\ \pi\ r^2\ \sigma$$

Graphing this as a function of radius shows that it costs free energy to add molecules to this cluster, until the radius reaches

$$r^* = \frac{2\sigma}{G_v}$$

Addition of new molecules to clusters larger than this critical radius releases, rather than costs, available work. In other words at that point growth of the cluster is no longer limited by nucleation, but perhaps by diffusion (i.e. the supply of molecules) or by reaction kinetics instead.

As the phase transformation becomes more and more favorable, the formation of a given volume of nucleus frees enough energy to form an increasingly large surface, allowing progressively smaller nuclei to become viable. Eventually, thermal activation will provide enough energy to form stable nuclei. These can then grow until thermodynamic equilibrium is restored.

The spontaneous nucleation rate in, say, water changes very rapidly with temperature, so the spontaneous nucleation temperature can be quite well defined. 'Film boiling' on very hot surfaces and the Leidenfrost effect are both believed to be stabilized by spontaneous nucleation phenomena.

Heterogeneous nucleation

In the case of heterogeneous nucleation, some energy is released by the partial destruction of the previous interface. For example, if a carbon dioxide bubble forms between water and the inside surface of a bottle, the energy inherent in the water-bottle interface is released wherever a layer of gas intervenes, and this energy goes toward the formation of bubble-water and bubble-bottle interfaces. The same effect can cause precipitate particles to form at the grain boundaries of a solid. This can interfere with precipitation strengthening, which relies on homogeneous nucleation to produce a uniform distribution of precipitate particles.

2- Crystal Growth

Crystal growth is a major stage of a crystallization process, after the nucleation stage. It occurs from the addition of new atoms, ions, or polymer strings into the characteristic arrangement, or lattice, of a crystal. Crystal growth spreads outwards from the nucleating site. In this faster process, the elements which form the motif add to the growing crystal in a prearranged system, the crystal lattice, started in crystal nucleation. As first pointed out by Charles Frank in 1951, perfect crystals would only grow exceedingly slowly; real crystals grow comparatively rapidly because they contain dislocations, which provide the necessary growth points.

The earliest crystal grower was nature. Many excellent crystals of minerals formed in the geologic past are found in mines and caves throughout the world. Most precious and semiprecious stones are well-formed crystals. Early efforts to produce synthetic crystals were concentrated on making gems. Synthetic ruby was grown by the French scientist Marc Antoine Augustin Gaudin in 1873. Since about 1950 scientists have learned to grow in the laboratory crystals of quality equal or superior to those found in nature. New techniques for growth are continually being developed, and crystals with three or more atoms per unit cell are continually being discovered.

There are numerous ways to grow crystals. The choice of method depends greatly upon the physical and chemical properties of the sample. For solution methods of crystallization, the solubility of the sample in various solvent systems must be explored. If heating methods are selected for growing crystals, the thermal stability and melting point of the sample should be determined.

There are a few general points that apply to all crystallization methods.

- It is important that the sample be as pure as possible. When crystallization attempts consistently yield oils, the sample is probably not pure. The solvents or cocrystallizing materials should be as pure as possible. Contaminants may often break down the desired sample.
- It is important for most solution methods that the glassware be thoroughly clean and "old" or "used." New glassware is so smooth that there are no nucleation sites available on the exposed surfaces. Also, new glassware from the manufacturer usually has a variety of dusty contaminants.
- If a sample only yields small crystals, the method should be altered so as to slow down the growth step. Slowing the crystal growth sometimes requires changing the method used to grow the crystals.
- Avoid vibrations near your growing crystals.
- Finally be patient! Some methods work in a few hours, and other methods require weeks or even months for success.

Conventional crystal growth techniques can be classified into the following categories:

- *Vapor growth*: Growth by evaporation and condensation or by chemical reaction.
- *Melt growth*: Growth by directional solidification of the melt, or by movement of a molten zone through a solid ingot of the material.
- *Solution growth*: Crystallization by cooling or evaporation of the solvent or growth from chemical reaction in the liquid phase.
- *Dendritic growth*.

2-1 Vapor Growth:

Crystals can be grown from a vapour when the molecules of the gas attach themselves to a surface and move into the crystal arrangement.

Several important conditions must be met for this to occur. At constant temperature and equilibrium conditions, the average number of molecules in the gas and solid states is constant; molecules leave the gas and attach to the surface at the same rate that they leave the surface to become gas molecules. For crystals to grow, the gas-solid chemical system must be in a nonequilibrium state such that there are too many gaseous molecules for the conditions of pressure and temperature. This state is called supersaturation. Molecules are more prone to leave the gas than to rejoin it, so they become deposited on the surface of the container. Supersaturation can be induced by maintaining the crystal at a lower temperature than the gas. A critical stage in the growth of a crystal is seeding, in which a small piece of crystal of the proper structure and orientation, called a seed, is introduced into the container. The gas molecules find the seed a more favourable surface than the walls and preferentially deposit there. Once the molecule is on the surface of the seed, it wanders around this surface to find the preferred site for attachment. Growth proceeds one molecule at a time and one layer at a time. The process is slow; it takes days to grow a small crystal. Crystals are grown at temperatures well below the melting point to reduce the density of defects. The advantage of vapour growth is that very pure crystals can be grown by this method, while the disadvantage is that it is slow.

Most clouds in the atmosphere are ice crystals that form by vapour growth from water molecules. Most raindrops are crystals as they begin descending but thaw during their fall to Earth. Seeding for rain—accomplished by dropping silver iodide crystals from airplanes—is known to induce precipitation. In the laboratory, vapour growth is usually accomplished by flowing a supersaturated gas over a seed crystal. Quite often a chemical reaction at the surface is needed to deposit the atoms.

Crystals of silicon can be grown by flowing chlorosilane ($SiCl_4$) and hydrogen (H_2) over a seed crystal of silicon. Hydrogen acts as the buffer gas by controlling the temperature and rate of flow. The molecules dissociate on the surface in a chemical reaction that forms hydrogen chloride (HCl) molecules. Hydrogen chloride molecules leave the surface, while silicon atoms remain to grow into a crystal. Binary crystals such as gallium arsenide (GaAs) are grown by a similar method. One process employs gallium chloride (GaCl) as the gallium carrier. Arsenic is provided by molecules such as arsenous chloride ($AsCl_3$), arsine (AsH_3), or As_4 (yellow arsenic). These molecules, with hydrogen as the buffer gas, grow crystals of gallium arsenide while forming gas molecules such as gallium trichloride ($GaCl_3$) and hydrogen chloride. Trimethylgallium, $(CH_3)_3Ga$, is another molecule that can be used to deliver gallium to the surface.

Epitaxy

Epitaxy refers to the method of depositing a monocrystalline film on a monocrystalline substrate. The deposited film is denoted as epitaxial film or epitaxial layer. The term epitaxy comes from a Greek root (*epi* "above" and *taxis* "in ordered manner") which could be translated to "arrange upon".

Epilayer is the outside or covering layer.

Epitaxial films may be grown from gaseous or liquid precursors. Because the substrate acts as a seed crystal, the deposited film takes on a lattice structure and orientation identical to those of the substrate. This is different from other thin-film deposition methods which deposit polycrystalline or amorphous films, even on single-crystal substrates. If a film is deposited on a substrate of the same composition, the process is called homoepitaxy; otherwise it is called heteroepitaxy.

Homoepitaxy is a kind of epitaxy performed with only one material. In homoepitaxy, a crystalline film is grown on a substrate or film of the same material. This technology is applied to growing a more purified film than the substrate and fabricating layers with different doping levels.

Heteroepitaxy is a kind of epitaxy performed with materials that are different from each other. In heteroepitaxy, a crystalline film grows on a crystalline substrate or film of another material. This technology is often applied to growing crystalline films of materials of which single crystals cannot be obtained and to fabricating integrated crystalline layers of different materials. Examples include gallium nitride (GaN) on sapphire or aluminium gallium indium phosphide (AlGaInP) on gallium arsenide (GaAs).

Heterotopotaxy is a process similar to heteroepitaxy except for the fact that thin film growth is not limited to two dimensional growth. Here the substrate is similar only in structure to the thin film material.

Epitaxy is used in silicon-based manufacturing processes for BJTs and modern CMOS, but it is particularly important for compound semiconductors such as gallium arsenide. Manufacturing issues include control of the amount and uniformity of the deposition's resistivity and thickness, the cleanliness and purity of the surface and the chamber atmosphere, the prevention of the typically much more highly doped substrate wafer's diffusion of dopant to the new layers, imperfections of the growth process, and protecting the surfaces during the manufacture and handling.

Molecular beam epitaxy

Molecular beam epitaxy (MBE), is one of several methods of depositing single crystals. It was invented in the late 1960s at Bell Telephone Laboratories by J. R. Arthur and Alfred Y. Cho.

Molecular beam epitaxy takes place in high vacuum or ultra high vacuum (10^{-8} Pa). The most important aspect of MBE is the slow deposition rate (typically less than 1000 nm per hour), which allows the films to grow epitaxially. The slow deposition rates require proportionally better vacuum to achieve the same impurity levels as other deposition techniques.

In solid-source MBE, ultra-pure elements such as gallium and arsenic are heated in separate quasi-knudsen effusion cells until they begin to slowly sublimate. The gaseous elements then condense on the wafer, where they may react with each other. In the example of gallium and arsenic, single-crystal gallium arsenide is formed. The term "beam" means that evaporated atoms do not interact with each other or vacuum chamber gases until they reach the wafer, due to the long mean free paths of the atoms.

During operation, RHEED (Reflection High Energy Electron Diffraction) is often used for monitoring the growth of the crystal layers. A computer controls shutters in front of each furnace, allowing precise control of the thickness of each layer, down to a single layer of atoms. Intricate structures of layers of different materials may be fabricated this way. Such control has allowed the development of structures where the electrons can be confined in space, giving quantum wells or even quantum dots. Such layers are now a critical part of many modern semiconductor devices, including semiconductor lasers and light-emitting diodes.

In systems where the substrate needs to be cooled, the ultra-high vacuum environment within the growth chamber is maintained by a system of cryopumps, and cryopanels, chilled using liquid nitrogen or cold nitrogen gas to a temperature close to 77 kelvins (−196 degrees Celsius). Cryogenic temperatures act as a sink for impurities in the vacuum, so vacuum levels need to be several orders of magnitude better to deposit films under these conditions. In other systems, the wafers on which the crystals are grown may be mounted on a rotating platter which can be heated to several hundred degrees Celsius during operation.

Molecular beam epitaxy is also used for the deposition of some types of organic semiconductors. In this case, molecules, rather than atoms, are evaporated and deposited onto the wafer. Other variations include gas-source MBE, which resembles chemical vapor deposition.

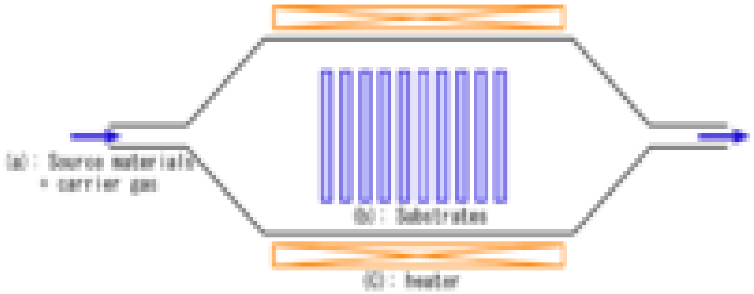
Chemical vapor deposition

Chemical vapor deposition (CVD) is a chemical process used to produce high-purity, high-performance solid materials. The process is often used in the semiconductor industry to produce thin films. In a typical CVD process, the wafer (substrate) is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit. Frequently, volatile by-products are also produced, which are removed by gas flow through the reaction chamber.

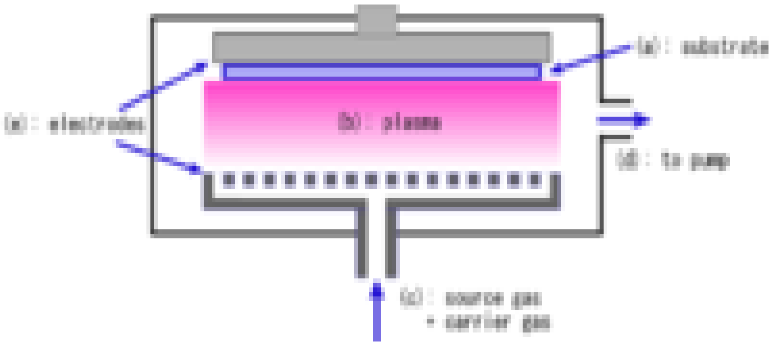
DC plasma (violet) enhances the growth of carbon nanotubes in this laboratory-scale PECVD apparatus.

Microfabrication processes widely use CVD to deposit materials in various forms, including: monocrystalline, polycrystalline, amorphous, and epitaxial. These materials include: silicon, carbon fiber, carbon nanofibers, filaments, carbon nanotubes, SiO_2, silicon-germanium, tungsten, silicon carbide, silicon nitride, silicon oxynitride, titanium nitride, and various high-k dielectrics. The CVD process is also used to produce synthetic diamonds.

Types of chemical vapor deposition



hot-wall thermal CVD (batch operation type)



plasma assisted CVD

A number of forms of CVD are in wide use and are frequently referenced in the literature. These processes differ in the means by which chemical reactions are initiated (e.g., activation process) and process conditions.

- Classified by operating pressure
  - *Atmospheric pressure CVD* (APCVD) - CVD processes at atmospheric pressure.

- *Low-pressure CVD* (LPCVD) - CVD processes at subatmospheric pressures. Reduced pressures tend to reduce unwanted gas-phase reactions and improve film uniformity across the wafer. Most modern CVD process are either LPCVD or UHVCVD.
- *Ultrahigh vacuum CVD* (UHVCVD) - CVD processes at a very low pressure, typically below 10^{-6} Pa (~ 10^{-8} torr). Caution: in other fields, a lower division between high and ultra-high vacuum is common, often 10^{-7} Pa.
- Classified by physical characteristics of vapor
- *Aerosol assisted CVD* (AACVD) - A CVD process in which the precursors are transported to the substrate by means of a liquid/gas aerosol, which can be generated ultrasonically. This technique is suitable for use with involatile precursors.
- *Direct liquid injection CVD* (DLICVD) - A CVD process in which the precursors are in liquid form (liquid or solid dissolved in a convenient solvent). Liquid solutions are injected in a vaporization chamber towards injectors (typically car injectors). Then the precursors vapors are transported to the substrate as in classical CVD process. This technique is suitable for use on liquid or solid precursors. High growth rates can be reached using this technique.
- Plasma methods (see also Plasma processing)
- *Microwave plasma-assisted CVD* (MPCVD)
- *Plasma-Enhanced CVD* (PECVD) - CVD processes that utilize a plasma to enhance chemical reaction rates of the precursors. PECVD processing allows deposition at lower temperatures, which is often critical in the manufacture of semiconductors.
- *Remote plasma-enhanced CVD* (RPECVD) - Similar to PECVD except that the wafer substrate is not directly in the plasma discharge

region. Removing the wafer from the plasma region allows processing temperatures down to room temperature.

- *Atomic layer CVD* (ALCVD) – Deposits successive layers of different substances to produce layered, crystalline films. See Atomic layer epitaxy.
- *Hot wire CVD* (HWCVD) - Also known as Catalytic CVD (Cat-CVD) or hot filament CVD (HFCVD). Uses a hot filament to chemically decompose the source gases.[1]
- *Metalorganic chemical vapor deposition* (MOCVD) - CVD processes based on metalorganic precursors.
- *Hybrid Physical-Chemical Vapor Deposition* (HPCVD) - Vapor deposition processes that involve both chemical decomposition of precursor gas and vaporization of solid a source.
- *Rapid thermal CVD* (RTCVD) - CVD processes that use heating lamps or other methods to rapidly heat the wafer substrate. Heating only the substrate rather than the gas or chamber walls helps reduce unwanted gas phase reactions that can lead to particle formation.
- *Vapor phase epitaxy* (VPE)

Vapor-phase Epitaxy

Silicon is most commonly deposited from silicon tetrachloride in hydrogen at approximately 1200 °C:

$$SiCl_{4(g)} + 2H_{2(g)} \leftrightarrow Si_{(s)} + 4HCl_{(g)}$$

This reaction is reversible, and the growth rate depends strongly upon the proportion of the two source gases. Growth rates above 2 micrometres per minute produce polycrystalline silicon, and negative growth rates (etching) may occur if too much hydrogen chloride byproduct is present. (In fact, hydrogen chloride may be added intentionally to etch the wafer.) An additional etching reaction competes with the deposition reaction:

$$SiCl_{4(g)} + Si_{(s)} \leftrightarrow 2SiCl_{2(g)}$$

Silicon VPE may also use silane, dichlorosilane, and trichlorosilane source gases. For instance, the silane reaction occurs at 650 °C in this way:

$$SiH_4 \rightarrow Si + 2H_2$$

This reaction does not inadvertently etch the wafer, and takes place at lower temperatures than deposition from silicon tetrachloride. However, it will form a polycrystalline film unless tightly controlled, and it allows oxidizing species that leak into the reactor to contaminate the epitaxial layer with unwanted compounds such as silicon dioxide.

VPE is sometimes classified by the chemistry of the source gases, such as hydride VPE and metalorganic VPE.

Physical vapor deposition

Physical vapor deposition (PVD) is a variety of vacuum deposition and is a general term used to describe any of a variety of methods to deposit thin films by the condensation of a vaporized form of the material onto various surfaces (e.g., onto semiconductor wafers). The coating method involves purely physical processes such as high temperature vacuum evaporation or plasma sputter bombardment rather than involving a chemical reaction at the surface to be coated as in chemical vapor deposition. The term physical vapor deposition appears originally in the 1966 book “Vapor Deposition *by CF Powell, JH Oxley and JM Blocher Jr, but Michael Faraday was using PVD to deposit coatings as far back as 1838.*

Variants of PVD include, in order of increasing novelty:

- Evaporative deposition: In which the material to be deposited is heated to a high vapor pressure by electrically resistive heating in "low" vacuum.

- Electron beam physical vapor deposition: In which the material to be deposited is heated to a high vapor pressure by electron bombardment in "high" vacuum.
- Sputter deposition: In which a glow plasma discharge (usually localized around the "target" by a magnet) bombards the material sputtering some away as a vapor.
- Cathodic Arc Deposition: In which a high power arc directed at the target material blasts away some into a vapor.
- Pulsed laser deposition: In which a high power laser ablates material from the target into a vapor.

PVD is used in the manufacture of items including semiconductor devices, aluminized PET film for balloons and snack bags, and coated cutting tools for metalworking. Besides PVD tools for fabrication special smaller tools mainly for scientific purposes have been developed. They mainly serve the purpose of extreme thin films like atomic layers and are used mostly for small substrates. A good example are mini e-beam evaporators which can deposit monolayers of virtually all materials with melting points up to 3500°C.

Some of the techniques used to measure the physical properties of PVD coatings are:

- Calo tester: coating thickness test
- Scratch tester: coating adhesion test
- Pin on disc tester: wear and friction coefficient test

Applications of Epitaxy

It has applications in nanotechnology and in semiconductor fabrication. Indeed, epitaxy is the only affordable method of high crystalline quality growth for many semiconductor materials, including technologically important materials as silicon-germanium, gallium nitride, gallium arsenide and indium phosphide.

Epitaxy is also used to grow layers of pre-doped silicon on the polished sides of silicon wafers, before they are processed into semiconductor devices. This is typical of power devices, such as those used in pacemakers, vending machine controllers, automobile computers, etc.

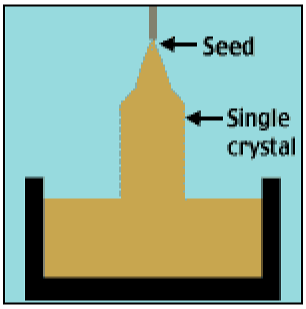
2-2 Melt Growth

Researches are being done now to improve the crystal growth of bulk, solid solution semiconductor materials from the melt using (Bridgman , Czochralski, zone refining, etc). These methods are used widely in the purification and growth of crystals of semiconductors and other electronic materials but are limited to compounds that melt without decomposition, thereby excluding many molecular compounds.

For growing crystals from melt the material to be grown in the forms of a single crystal is placed in a suitable container and heated in a furnace above the melting point. To initiate the growth the melt is cooled from above the equilibrium state in which the substance is completely molten above the melting point to a state such that the system is completely solid below the melting point. The crystal grower’s problem is to control this transition so that single crystal may grow. This is achieved by permitting at a time a small volume of the melt to pass through the transition temperature to crystallize. A temperature gradient is also necessary with one portion of the system above and the other portion below the melting point having a uniform temperature gradient. The rate at which the gradient moves through the system can be controlled so that the new melt, which is made labile with respect to growth, is restricted. Usually controlling the thermal gradient successfully controls the crystal growth from pure melt.

1- Czochralski Crystal Growth Method

The Czochralski method is a technique for growing single-crystal silicon ingots for use in manufacturing semiconductor devices. The finished crystals are called boules. The boules are later sliced into very thin, circular wafers and then diced into the little silicon chips from which all silicon semiconductor LSI chips are made.

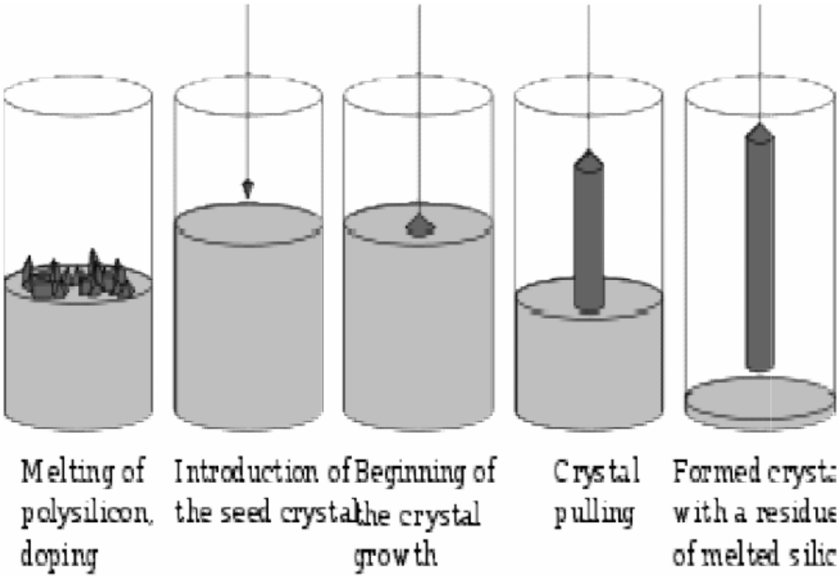


Growing large monocrystalline silicon boules is a tricky business. The Czochralski method (abbreviated as CZ in the technical literature) begins with silicon powder that is 99.999999999% pure. A lot of that ridiculously pure silicon is placed in a large crucible that is made of fused quartz. The crucible is then put in a vacuum chamber, which is sealed and then filled with some conveniently inert gas, usually argon.

The chamber is then heated up to 1500° Centigrade or so, to melt the silicon. When the silicon is nicely 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 red-hot silicon melt. The shaft rotates counterclockwise and the crucible rotates clockwise. Now, the rotating rod is drawn upwards very slowly, allowing a roughly cylindrical boule to form by some technical magic as it does so. The boule can be from one to two metres or so long, depending on how much silicon there is in the crucible.

In the early days of the technology, the boules were quite thin, only a few inches wide. However, the crystal growers have had a lot of practice, and nowadays they can make nice, fat 300mm (12-inch) wide boules. The thickness is controlled by precise control of the temperature, the speeds of rotation and how fast the seed holder is withdrawn. Widths of 400mm (16 inches) are expected in the next several years. This is one reason for the rapidly decreasing cost of chips that we have enjoyed over the years, because more LSI chips can be created from a single wafer with the same number of fabrication process steps.

Czochralski process

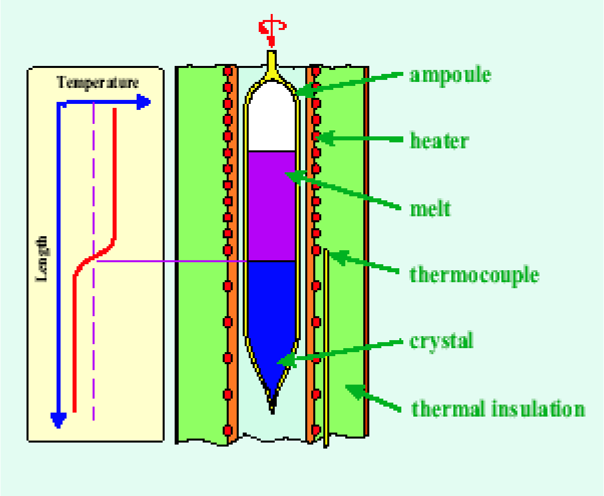


High-purity, semiconductor-grade silicon (only a few parts per million of impurities) is melted down in a crucible , which is usually made of quartz. Dopant impurity atoms such as boron or phosphorus can be added to the molten intrinsic silicon in precise amounts in order to dope the silicon, thus changing it into n-type or p-type extrinsic silicon. This influences the electrical conductivity of the silicon. A *seed crystal*, mounted on a rod, is dipped into the molten silicon. The seed crystal's rod is pulled upwards and rotated at the same time. By precisely controlling the temperature gradients, rate of pulling and speed of rotation, it is possible to extract a large, single-crystal, cylindrical ingot from the melt. Occurrence of unwanted instabilities in the melt can be avoided by investigating and visualizing the temperature and velocity fields during the crystal growth process. This process is normally performed in an inert atmosphere, such as argon, and in an inert chamber, such as quartz.

puller rod with seed crystal for growing single-crystal silicon by the Czochralski process

2- The Vertical Bridgman Stockbarger Technique (VBS)

Many named variations exist, such as Bridgman, Stockbarger, Tamman and Stober techniques. The basic principle of all these is the same. In the vertical Bridgman Stockbarger technique (VBS) the melt is contained in a vertically mounted crucible with a sharp point at the bottom.

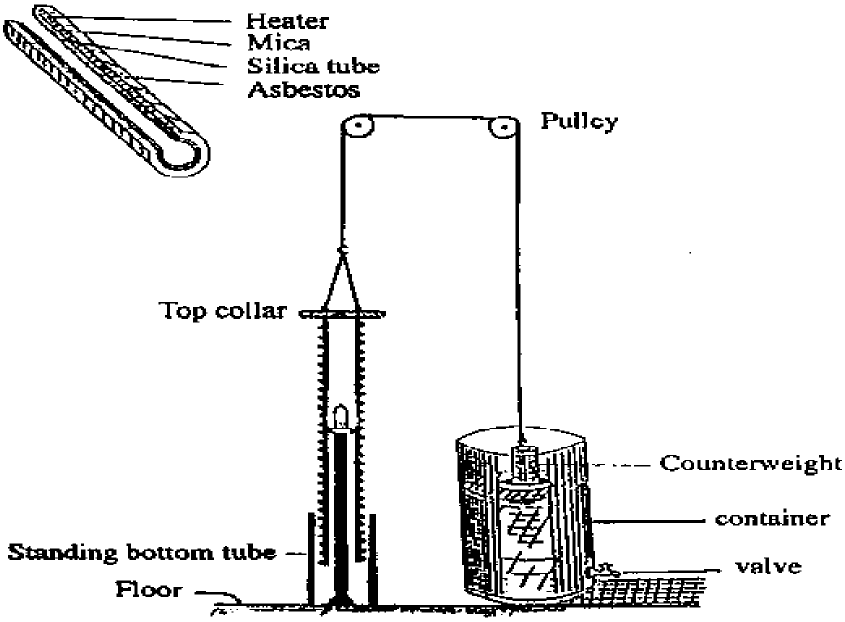


The crucible is lowered mechanically through a freezing plane so that solidification starts at the point at the bottom. The rats of movement for such processes range from 0.1 to 200 mm/h. The shape of the pointed end is such that a small single crystal often forms and provides a seed for the remainder of the melt. This technique is remarkably successful for some materials. The crucible is normally sealed off at the top to prevent atmospheric contamination but clearly this cannot be done when the constituents of the melt have high vapor pressures.

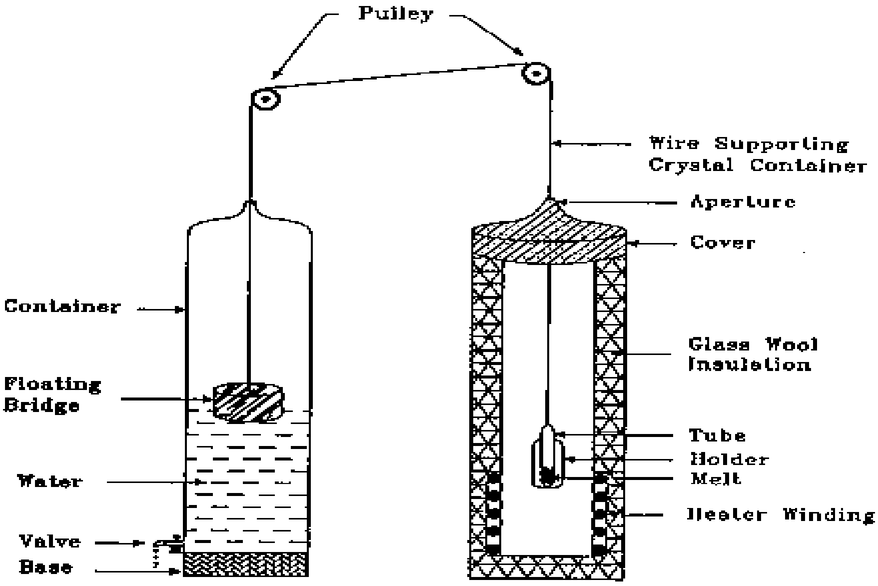
The lowering rate should be slow enough to permit all the heat of crystallization to be conducted away down through the crystal. In such cases the solid melt interfaces is maintained planer and horizontal.

Local Modifications of Melt Crystals Growth Techniques

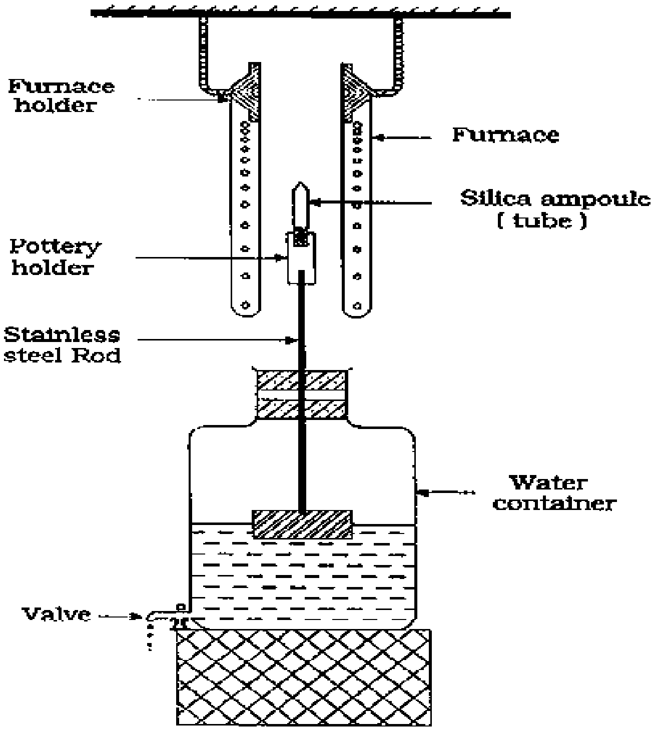
From the point of view of vibration it is better to move the furnace than the crystal. In this case the technique is called the traveling heater method (THM). Another attempt to improve this technique for THM. The main advantage of this technique is that it causes no vibrations to the melt.



However the main problem in such techniques is the absence of the smooth and accurate graduation of temperature, which is the main reason for coherent and incoherent, precipitates. The present design is a modification of the traveling solvent method (TSM) technique. The main advantage of this technique is that the temperature gradient is granted.



A recent modification has been achieved in our laboratory .



Beside the above advantages involved in the previous techniques, the present technique introduces a suitable solution to the presence of the pulleys and hence their problems. Where in this apparatus the ampoule, with its charge, is supported in its holder and the whole are placed in a three-zone tube furnace. Here it’s seen that the furnace is fixed and the ampoule is movable with the required rate with the aid of hydraulic driving force.

Detached Crystal Growth

2.1.3 Crystal Quality and Growth Conditions

Crystal quality improves with experience, and early attempts often produce poor quality crystals. It is important to continue until it is clear that no further improvement is likely. In some cases, regardless of the method employed, crystals either do not form or are unsuitable. The material is often precipitated very rapidly, resulting in microcrystalline or virtually amorphous products that are useless for conventional single crystal work. The object is to obtain relatively large single crystals. As long as this yield is irrelevant and purity is likely to be enhanced. To this end crystals should be slowly, taking from minutes to months depending on the system. To understand why this is important, visuals the process of growth at a crystal surface. The greater the rate at which molecules arrive at the surface, the less time they have to orient themselves in relation to molecules already there, random accretion is more likely leading to crystals which are twinned or disordered. Suitable growth conditions include the absence of dust and vibrations; if these are present they can lead to crystals, which are small or non-singular.

2.1.5 Disadvantages of Crucible in Bridgman Growth

In the vertical Bridgman Stockbarger technique (VBS) the melt is contained in a vertically mounted crucible with a sharp point at the bottom. The crucible is lowered mechanically through a freezing plane so that solidification starts at the point at the bottom. The rats of movement for such processes range from 0.1 to 200 mm/h. The shape of the pointed end is such that a small single crystal often forms and provides a seed for the remainder of the melt. This technique is remarkably successful for some materials. The crucible is normally sealed off at the top to prevent atmospheric contamination but clearly this cannot be done when the constituents of the melt have high vapor pressures. The crucible is necessary to support the melt, because, in contrast to the float-zone method, the whole feed material (above the crystal) is molten. Different expansion properties between the ampoule and crystal lead to undesirable defects in the grown material during the growth process. These defects can be reduced if the grown crystal is not in contact with the ampoule material. Under microgravity conditions semiconductor crystals were reproducibly obtained without contact with the crucible. The phenomenon is described in the literature as “detached growth” in the general case and as “dewetted growth” when the gap between the crystal and the crucible is constant and very small (some tens of micrometers).

Under special conditions the melt at the liquid/solid interface is detached from the wall and the crystal grows without contact. Growth under such conditions is known as detached Bridgman growth (dB). Detachment can be influenced by parameters like gravitational force, ampoule material (determines the contact angle between the container and the melt), and pressure forces above and below the melt.

2.1.6 Detachment Phenomenon

Directional solidification in microgravity has often led to ingots that grew with little or no contact with the ampoule wall. When this occurred, crystallographic perfection was usually greatly improved often by several orders of magnitude. Indeed, under the Soviet microgravity program the major objective was to achieve detached solidification with its resulting improvement in perfection and properties. As a consequence, flight experiments yielded erratic results. Unfortunately, until recently the true mechanisms underlying detached solidification were unknown. Over the past 30 years, several models have been proposed to explain detached solidification. Beginning with Skylab in 1974, many investigators found directional solidification in microgravity often yielded ingots that appear to have grown without being in intimate contact with their containers. Detached solidification has been observed at both fast and slow freezing rates. Sometimes it occurred with one type of dopant and not with others. The type of detachment, indeed even whether detachment occurred or not, has not been reproducible. Wide ranges of surface features and behavior have been observed. These features had classified into the categories shown below. Note that a given ingot might display several of these features along its length, but not all of them.

1- The ingot easily slid out of its container, whereas sticking was observed when solidification was carried out on earth under otherwise identical conditions.

2- On its surface, the ingot had isolated voids or bubbles of various sizes, depths and contact angles with the ampoule wall.

3- With a triangular or rectangular cross – section ampoule, the ingot had cylindrical detached surfaces in the corners and flat surfaces in contact the wall over most of each face.

4- With an ampoule containing grooves machined in it, the ingot contacted only the peaks of the grooves.

5- After correcting of thermal contraction, there remained a gap of about 1 to 60 μm between the ingot and the ampoule wall around the entire periphery.

6- There was a gap of up to several mm between the ingot and the wall, typically with a wavy surface and sometimes forming an hourglass – shaped neck adjacent to the seed. Although this gap generally extended around the entire periphery, sometimes it was confined to a portion of the surface.

2.1.7 Explanation of the Detachment Phenomenon

2.1.7.1 Existence of the Gap

The basic idea is that between the grown crystal and ampoule wall a liquid meniscus exists and its shape is influenced only by the surface tension force and gas pressure in the hot and cold parts of the ampoule (see Fig. 2.7).

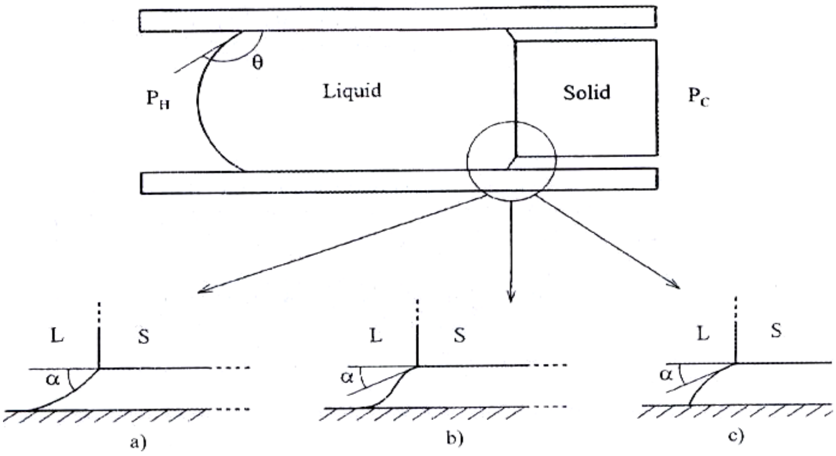


Fig. 2.7

1) <u>At equal gas pressure</u> between the hot and cold sides of the liquid, the curvature of the hot and cold liquid surfaces is the same and the gap exits at:

$$\theta + \alpha > \pi \qquad 2\text{-}1$$

where θ is the wetting angle of the liquid on the crucible and α the growth angle of the crystal material (Fig. 2-2 – a). The thickness of the gap is:

$$e = r\,\{(\cos\theta + \cos\alpha) / \cos\theta\,\} \qquad 2\text{-}2$$

with r the internal radius of the crucible. However the largest growth angle ever reported for semiconductors is 30o, in the case of InSb, and Young’s (thermodynamic) wetting angle hardly reaches the value of 140^o. Therefore the condition $\theta + \alpha > \pi$ is difficult to fulfill, except if some pollution of the liquid or solid surfaces can lead to an increase of these angles.

2) <u>At different gas pressure</u> at the hot and cold sides of the liquid the shape of the meniscus is more complicated (Fig. 2.7, b and c), but nevertheless dewetting has been observed. Popov et al. have shown that the gas dissolved in the liquid can release due to its rejection at the solid – liquid interface and this causes the detachment growth. They gave qualitative and quantitative arguments for an explanation of the phenomenon. In particular, they show that the gap thickness is depending on the growth rate.

The gas exchanges can occur through the channel between the hot and cold sides of the liquid. This situation observed several times when samples have been grown in cylindrical tubular crucibles opened at both ends.

2.1.7.2 Stability of the Detached Growth

The growth is stable if the meniscus curvature is positive (convex shape). The analytic expression for the stability can be written as function of the angle β between the normal to the liquid surface and the axis of symmetry:

$$\left(\frac{\partial \beta}{\partial x}\right)_{x=r-r_o} > 0 \qquad \text{2-3}$$

This is true not only if the geometrical stability alone is taken into account but also if heat transfer in the system is considered.

The pressure difference between the gas at the cold side of the ampoule, P_c, and at the hot side, P_h , is defined by Laplace’s equation:

$$\Delta \mathrm{P} = P_h - 2\frac{\delta}{b} + \rho g(H-z) - P_c \qquad \text{2-4}$$

where δ is the liquid surface tension, the 2 δ / b term is the contribution due to the curvature b at the top of the free liquid. ρg(H-z) is the gravity contribution with H the total height of the liquid. It is possible to compute numerically the meniscus shape and it follows that the shape is not changing during the solidification process, if:

$$P_c - P_h - \rho g H = \text{constant} \qquad \text{2-5}$$

Under microgravity this condition is simply described by the pressure difference between the cold and hot areas $P_c - P_h$. Then if it remains constant, and if Eq.2-3 is fulfilled, the gap thickness is stable and constant all along the growth.

On earth, the stability of the system is depending on a linear variation with the solidified length because of the decrease of the hydrostatic pressure.

In summary:

- If the gas pressure is equilibrated throughout the ampoule, some pollution of the sample and crucible surfaces should explain the dewetting phenomenon. If this factor of pollution is constant during the growth, then the stability of the dewetting process can be easily explained.

- If there is a positive gas pressure difference between cold and hot sides of the liquid, then Eq.2-3 should be fulfilled and all the parameters (thermal gradient, growth rate) should remained constant during the dewetting growth.
- If the gas pressures difference between the cold and hot sides of the liquid is negative, then the dewetting growth is not possible to achieve.

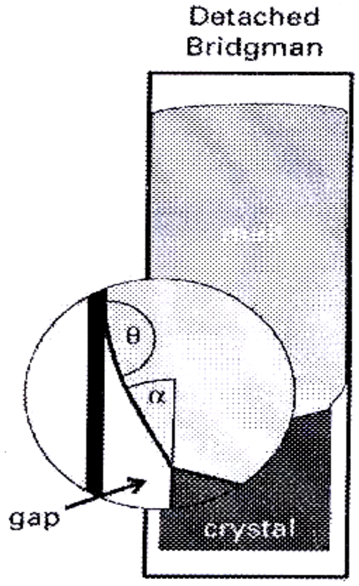
2.1.8 Parameters and Factors Promoting Detachment Growth

Although the mechanism of detached growth is not yet clear in all details, there is a common understanding about the main factors playing an important role for the appearance of detached growth:

1- *Gravity*: A common feature of nearly all the growth processes where detachment was observed was the fact that the experiments were performed under microgravity. Under normal gravity, the liquid might be pressed into the gap between crystal and crucible due to the hydrostatic pressure and the shape of the meniscus is influenced in an undesirable way. A second point is the convective mixing of the melt under 1 *g* (where *g* is the gravity of earth) conditions prevent the accumulation and evaporating of the rejected gas at the solid – liquid interface.

2- *Wetting angle*: The gap thickness and the stability of the wall – free growth depend on the wetting behavior between the melt and the container material (expressed through the contact angle θ).

3- *Growth angle*: The growth angle α of the crystal, and external forces, which can change the meniscus shape of the growing crystal. Without consideration of external force, detachment will occur if the sum of the wetting angle and growth angle equal or larger than 180^o, which follows from geometrical consideration (see Fig. 2.8).



4- *Growth velocity*: Growth velocity in the system may retard or enhance the detachment. Usually the detachment is observed with slow velocities.

5- *Pressure:* It is suggested to keep a high enough pressure below the meniscus to counterbalance the hydrostatic pressure of the volume above it **[95]**. Several techniques to establish this pressure have been proposed, whereas in more recent works the pressure was indirectly controlled via the temperature field. However, when the wetting angle is high, detachment can still occur even if the pressure difference above and below the meniscus is zero.

6- *Inert gas:* The inert gas which usually present in the environment to protect the growth and is dissolved in the melt, gets rejected at the growth interface and transported to the sides of the crystals because of a radial gas concentration gradient. Then accumulation of the rejected gas between the solid crystal and the crucible eventually creates a pressure pushing the liquid away from the crucible wall, creating the meniscus.

7- *Melt contaminants*: Any impurity in the system can modify the wetting between the melt and its container. In addition, based on the reaction product between the impurity and the melt (or crucible), detachment can be hindered or enhanced.

8- *Growth atmosphere:* Growth atmosphere affects the detachments via changing the surface characteristics of the melts and crucibles, small melt – gas surface tension has been predicted to promote detachment.

9- *Interface reaction:* Interface reactions at the solid / liquid (s/l) interface are very important, giving rise to wetting or non-wetting. For example, carbon in contact with metallic melts interacts with outer 2p and 3p electrons of the melt. This interaction forms a covalent bond between carbon and the metallic melt such as B and Si. However, for elements with the main quantum number of $n = 4$ or greater (e.g. Ge) the metallic melt is practically inert to carbon.

10- *Crucible surface:* Duffar et al. pointed out that *Rough Crucibles* support detachment or at least reduce the melt area which is in contact with the crucible and lead therefore to reduce melt contamination, but the remaining ridges that can give rise to secondary nucleation, twins, and grains.

11- *Volatile Impurities:* Wilcox and Rege*l* reported that detachment is supported or even initiated by the gas pressure due to the rejection of *Volatile Impurities* at the solid – liquid interface and liberation of these impurities through the meniscus into the gap between crystal and ampoule.

12- There was an optimal heater temperature range for the formation and growth gas bubbles. If the temperature of the heater was below a critical level (critical value depends on the other physical and operating conditions), many gas bubbles were trapped in the crystal and on the ampoule wall. On the other hand, if the heater temperature was above a critical level, no bubbles and tubes were trapped in the crystal or on the ampoule wall.

13- *The growth technique:* the buoyancy – driven convection and the stability of steady – state detachment were affected by the methods of crystal growth (Czocharlski growth, vertical Bridgman growth, horizontal Bridgman growth…).

14- *Aging of ampoule:* we must take in mind the time period between filling the ampoule with materials and starting growth method, the shortest possible delay between ampoule filling and growth experiment is 5 months.

15- *Type of the seed:* it is observed that when crystals grow from a conical initial geometry, a liquid meniscus cannot sustain during growth, leading to attached crystal growth. In contrast, when the crystals grow from a round seed, a gap between the seed and crucible can form, leading to a liquid meniscus between the crucible and the crystal.

16- *Rotation of the ampoule*: rotation of the ampoule did not favor the formation of gas bubbles or gas tubes.

2.1.9 Advantages of Detached Growth

1) Optimize the crystal quality.
2) Sticking of the crystal to the crucible wall and any related effects such as parasitic seed formation are excluded.
3) Thermal expansion of the crucible – crystal system can be avoided.
4) It led to less contamination of the melt by the crucible material.
5) Thermal and mechanical stresses due to inhomogeneous heat conductivity can be reduced.
6) Dislocations density was typically reduced by two orders of magnitude.
7) Reduced nucleation of grains and twins at the ampoule wall.
8) In semiconductors, charge carrier mobility was greatly increased.

2.2.1 Crystal Growth Requirements

A more fundamental difficulty with the melt growth method arises from the constraint imposed on the growing crystal by the crucible. Some materials expand on solidification and this can lead to strain in the crystal or even fracture of the crucible.

The most desirable characteristic of a crucible is that:

1- Presence of it should not contaminate the crystals.
2- Of high melting point and should stable along the temperature range.
3- Crucible compatible in principle can be rendered useless by reactions involving the atmosphere.
4- Crucibles should have a smaller coefficient of thermal conductivity than the crystal.
5- Crucibles should have tapered tips Fig. 2.9.

The crucible may be a glass or quartz tube with a capillary end containing the seed, as shown in Fig. 2.9. The shape of the tube is important to the prevention of twinning. It has been suggested that only the configurations of tips (a), (c), and (d) of Fig. 2.9 yield true monocrystals. The conical capillary should have a vertex angle of 45^{o} to 60^{o}, and the spiral must have not less than a one-half turn.

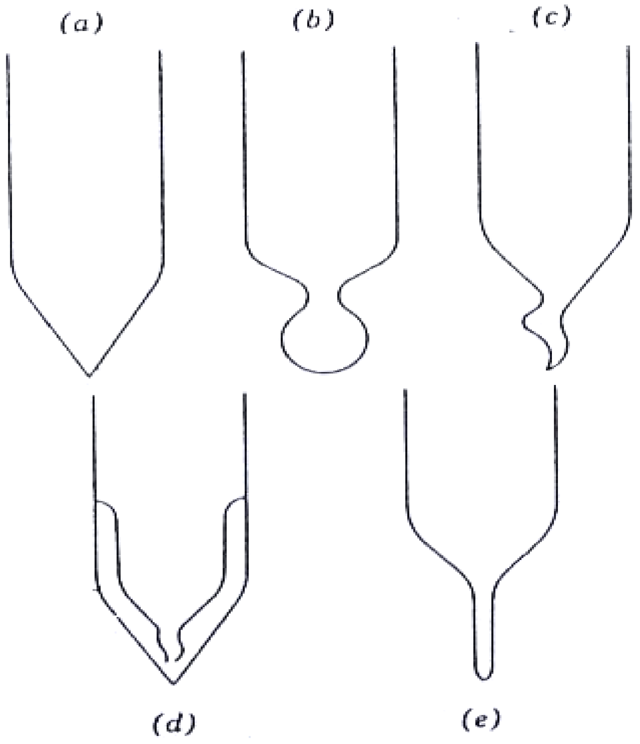


Fig. 2.9

Crucibles of various materials are used. Quartz **[120]** has a very low coefficient of thermal expansion (5.8 ×10-7) and a high softening point (quartz were may be heated up to 1300 ^{0}C without noticeable deformation). Quartz transmits not only rays of the visible spectrum, but also ultraviolet and infrared rays. It is one of the best dielectrics. Quartz is inert to acids and water. Silica is most useful as the crystal can be completely enclosed and sealed off so that no contamination or loss of vapor is possible. Silica coated with graphite is also used. Glass is used for low melting point materials and organic compounds. Graphite, carbon, platinum and several other refractory oxides have also been used.

Also the crystal growth process requires phase relation and phase diagram and the driving force for crystallization.

2.2.2 Crystal Growth Procedures

Many growth procedures were done before we have the product crystal. The following is a sum up for this work.

2.2.2.1 Ampoule Cleaning

Before the starting material was loaded into the ampoule (silica tube), the ampoule was cleaned by the following procedure:

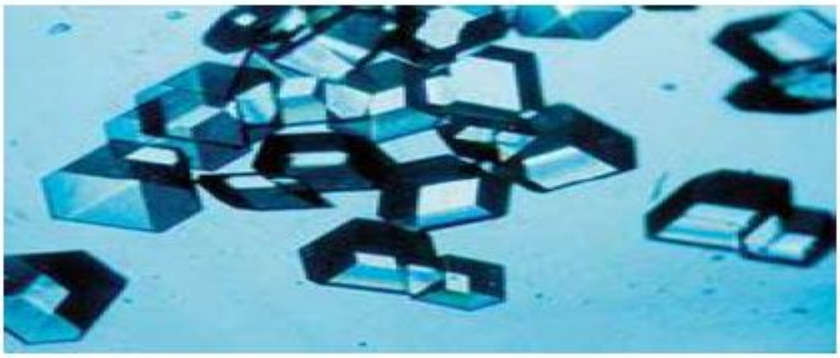
1. Soaked overnight in detergent solution.
2. Washed thoroughly in bidistilled water.
3. Rinsed with methanol and acetone.
4. Rinsed with bidistilled water 2 – 3 times.
5. Soaked in aqua regia for 1.5 hours.
6. Rinsed with bidistilled water.
7. Dried in an oven overnight at about 100 – 120 ^{o}C.

2.2.2.3 Evacuation and Sealing

The growth ampoule containing the charge was evacuated using a mechanical pump. The outlet valve of the chamber connected to this pump was 9 mm x 11 mm. The ampoule attaches this chamber via silica-fused tube, which in turn was connected to vacuum rubber tube. The ampoule was attached to the other end of this tube. The ampoule was evacuated to about 10 $^{-5}$ Torr.

The ampoules were prepared six months before put in furnace. The shortest possible delay between ampoule filling and microgravity experiments is five months.

Recrystallization



Insulin crystals

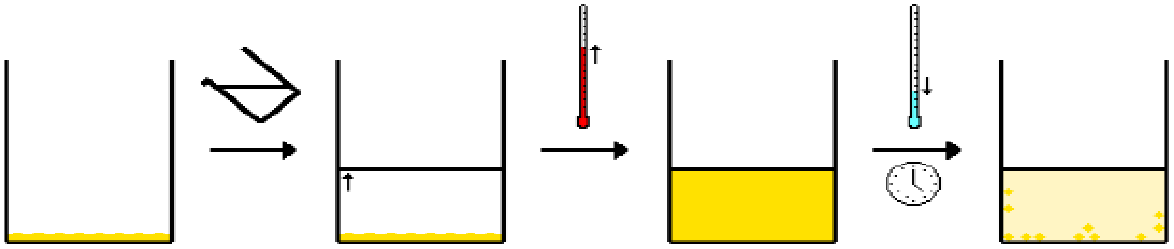
Recrystallization is a physical process that has meanings in chemistry, metallurgy and geology.

Chemistry

In chemistry, recrystallization is a procedure for purifying compounds. The most typical situation is that a desired "compound A" is contaminated by a small amount of "impurity B". There are various methods of purification that may be attempted (see Separation process), which includes recrystallization. There are also different recrystallization techniques that can be used such as:

Single-solvent recrystallization

Typically the mixture of "compound A" and "impurity B" are dissolved in the minimum amount of solvent to fully dissolve the mixture i.e. a saturated solution. The solution is then allowed to cool. As the solution cools the solubility of compounds in solution drops. This results in the desired compound dropping (recrystallizing) from solution. The slower the rate of cooling, the bigger the crystals formed.



→ Solvent added (clear) to compound (orange) → Solvent heated to give saturated compound solution (orange) → Saturated compound solution (orange) allowed to cool over time to give crystals (orange) and a non-saturated solution (pale-orange).

Crystallization of Ibuprofen in HCl(aq)

The crystallization process requires an initiation step. Once a small crystal has formed, more crystals can grow from that crystal. Since "Compound A" is in excess this will usually result in these crystals forming first and thus leaves a greater ratio of impurity in solution. Thus the resulting solid is more pure than the original mixture.

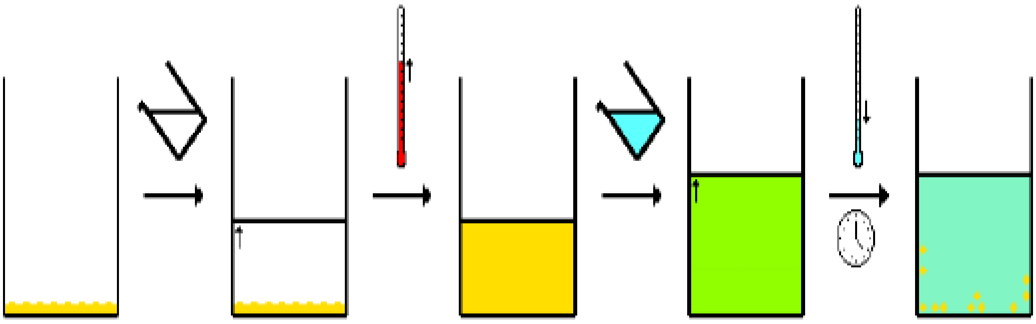
The level of purity can then be checked by taking a melting point range of the solid and comparing it to an accepted melting point range if one exists. Compounds that are more pure have higher accuracy in melting points and melt over a narrower temperature range. Obviously other analytical techniques can be used to assess compound purity such as NMR spectroscopy and elemental analysis.

This purification technique results in the inevitable loss of the part of "compound A" that remains in solution. A yield of 80% would be considered quite good. However the impure solution can be concentrated and the procedure repeated to gather a "second crop" of crystals.

Successful recrystallization depends on finding the right solvent. This is usually a combination of prediction/experience and trial/error. The mixture must be soluble at higher temperatures, and must be insoluble (or have low solubility) at lower temperatures.

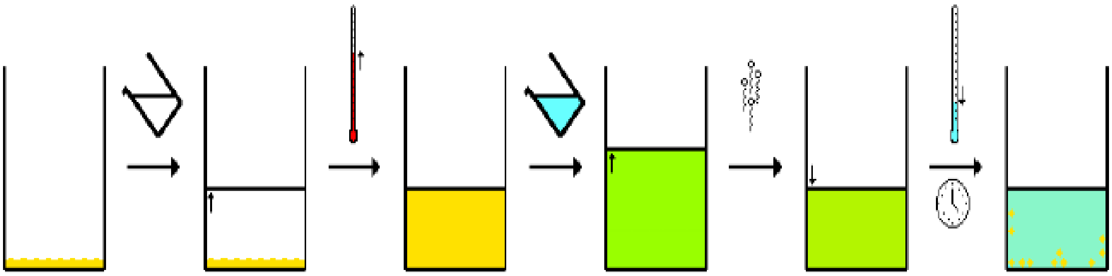
Multi-solvent recrystallization

This method is the same as the above but where two (or more) solvents are used. This relies on both "compound A" and "impurity B" being soluble in a first solvent. A second solvent is slowly added. Either "compound A" or "impurity B" will be insoluble in this solvent and precipitate, whilst the other of "compound A"/"impurity B" will remain in solution. Thus the proportion of first and second solvents is critical. Typically the second solvent is added slowly until one of the compounds begins to crystallize from solution and then the solution is cooled. Heating is not required for this technique but can be used.



→ Solvent added (clear) to compound (orange) → Solvent heated to give saturated compound solution (orange) → Second solvent (blue) added to compound solution (orange) to give mixed solvent system (green) → Mixed solvent system (green) allowed to cool over time to give crystals (orange) and a non-saturated mixed solvent system (green-blue).

The reverse of this method can be used where a mixture of solvent dissolves both A and B. One of the solvents is then removed by distillation or by an applied vacuum. This results in the a change in the proportions of solvent causing either "compound A" or "impurity B" to precipitate.



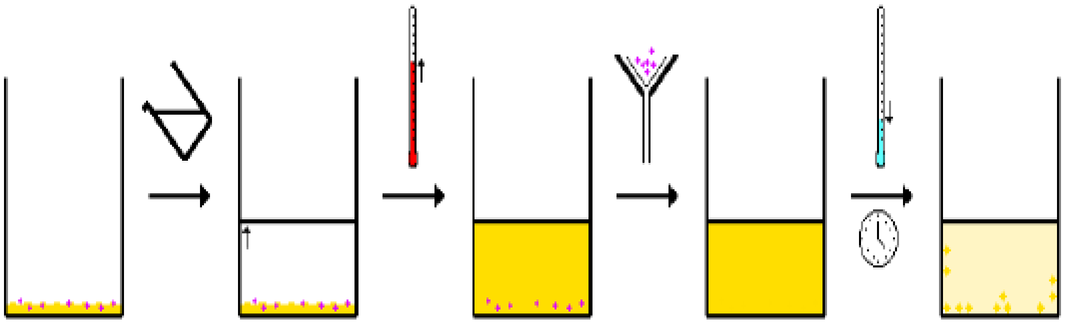
→ First solvent added (clear) to compound (orange) → Solvent heated to give saturated compound solution (orange) → Second solvent (blue) added to compound solution (orange) to give first mixed solvent system (green) → Volatile first solvent (clear) is removed (e.g. evaporation) from first mixed solvent system (green) to give a second mixed solvent system (dark-green) → Second mixed solvent system (dark-green) allowed to cool over time to give crystals (orange) and a non-saturated second mixed solvent system (green-blue)

Hot filtration-recrystallization

Hot filtration can be used to separate "compound A" from both "impurity B" and some "insoluble matter C". This technique normally uses a single solvent system as described above. When both "compound A" and "impurity B" are dissolved in the minimum amount of hot solvent, the solution is filtered to remove "insoluble matter C". This matter may be anything from a third impurity compound, to fragments of broken glass. For a successful procedure one needs to ensure that the filtration apparatus is hot to stop the dissolved compounds crystallizing from solution during the filtration step thus forming crystals on the filter paper or funnel.

One way of doing achieving this is to heat a conical flask containing a small amount of clean solvent on a hot plate. A filter funnel is rested on the mouth, and hot solvent vapors keep the stem warm. Jacketed filter funnels may also be used. The filter paper is preferably fluted, rather than folded into a quarter; this allows quicker filtration, thus less opportunity for the desired compound to cool and crystallize from the solution.

Often it is simpler to do the filtration and recrystallization as two independent and separate steps. That is dissolve "compound A" and "impurity B" in a suitable solvent at room temperature, filter (to remove insoluble compound/glass), remove the solvent and then recrystallize using any of the methods listed above.



→ Solvent added (clear) to a mixture of compound (orange) + insoluble substance (purple) → Solvent heated to give saturated compound solution (orange) + insoluble substance (purple) → Saturated compound solution (orange) filtered to remove insoluble substance (purple) → Saturated compound solution (orange) allowed to cool over time to give crystals (orange) and a non-saturated solution (pale-orange).

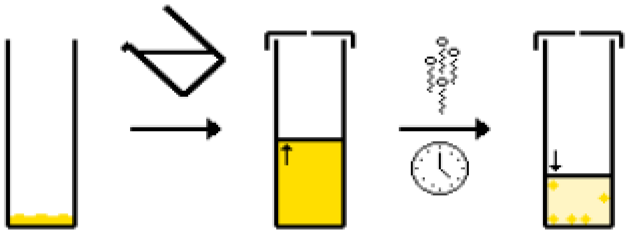
Seeding

Crystallization requires an initiation step. This can be spontaneous or can be done by adding a small amount of the pure compound (a seed crystal) to the saturated solution, or can be done by simply scratching the glass surface to create a seeding surface for crystal growth. It is thought that even dust particles can act as simple seeds.

Single perfect crystals (for X-ray analysis)

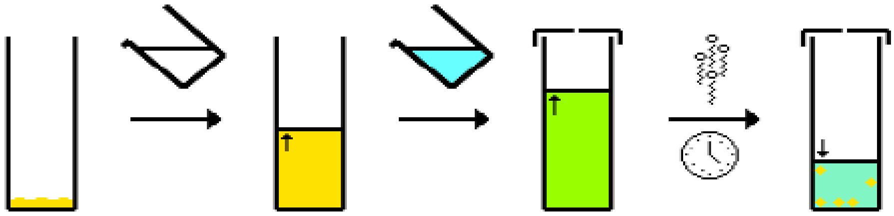
Growing crystals for X-ray crystallography can be quite difficult. For X-ray analysis, single perfect crystals are required. Typically a small amount (5-100 mg) of pure compound is used, and crystals are allowed to grow very slowly. Several techniques can be used to grow these perfect crystals:

- Slow evaporation of a single solvent - typically the compound is dissolved in a suitable solvent and the solvent is allowed to slowly evaporate. Once the solution is saturated crystals can form.



→ Solvent added (clear) to compound (orange) to give compound solution (orange) → Vessel sealed but a small hole allows solvent vapour (clear) to slowly evaporate from compound solution (orange) over time to give crystals (orange) and a non-saturated solution (pale-orange).

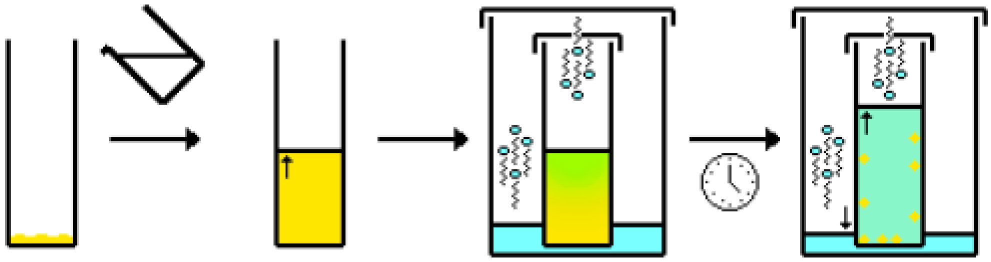
- Slow evaporation of a multi-solvent system - the same as above, however as the solvent composition changes due to evaporation of the more volatile solvent. The compound is more soluble in the volatile solvent, and so the compound becomes increasingly insoluble in solution and crystallizes.



→ Solvent added (clear) to compound (orange) to give compound solution (orange) → Second solvent added (blue) to compound solution (orange) to give mixed solvent system (green) → Vessel sealed but a small hole allows solvent vapour (clear) to slowly evaporate over time to give crystals (orange) and a non-saturated mixed solvent solution (blue-green)

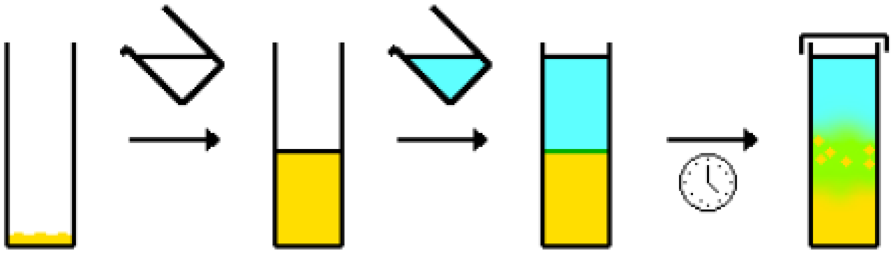
.

- Slow diffusion - similar to the above. However, a second solvent is allowed to evaporate from one container into a container holding the compound solution (gas-diffusion). As the solvent composition changes due to an increase in solvent that is has gas-diffused into solution, the compound become increasingly insoluble in solution and crystallizes.



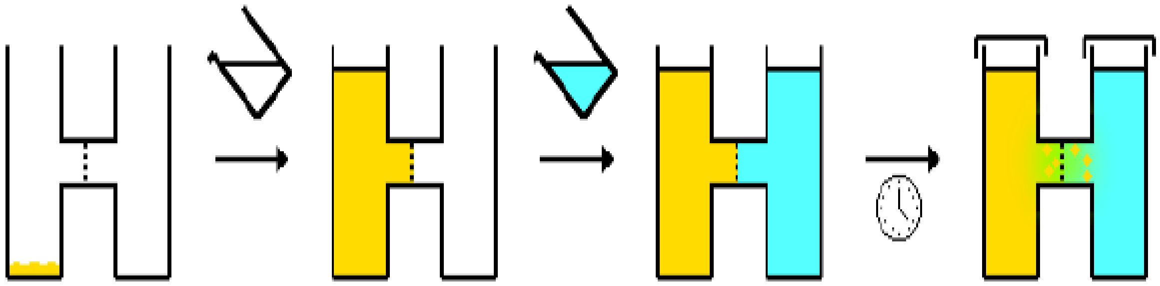
→ Solvent added (clear) to compound (orange) in first vessel to give compound solution (orange) → First vessel is placed in a second vessel contain second solvent (blue). The second vessel is sealed, the first vessel is also sealed, although a small hole in the first vessel is present. This hole allows volatile solvent vapour (blue) to slowly evaporate from second vessel and condensate (that is infuse) into the first vessel, to give a mixed solvent system (green) → Over time this gives crystals (orange) and a non-saturated mixed solvent system (green-blue).

- Interface/slow mixing (often performed in an NMR tube). Similar to the above, but instead of one solvent gas-diffusing into another, the two solvents mix (diffuse) by liquid-liquid diffusion. Typically a second solvent is "layered" carefully on top of the solution containing the compound. Over time the two solution mix. As the solvent composition changes due to diffusion, the compound becomes increasingly insoluble in solution and crystallizes, usually at the interface.



→ Solvent added (clear) to compound (orange) to give compound solution (orange) → Second solvent added (blue) carefully so that the two solvents do not mix. → The two solvents mix (diffuse) slowly over time to give crystals (orange) at solvent interface (green)

- Specialized equipment can be used in the shape of a "H" to perform the above, where one of the vertical line of the "H" is a tube containing a solution of the compound, and the other vertical line of the "H" is a tube containing a solvent which the compound is not soluble in, and the horizontal line of the "H" is a tube which joins the two vertical tubes, which also has a fine glass sinter that restricts the mixing of the two solvents.



→ Solvent added (clear) to compound (orange) to give a compound solution (orange) → Second solvent added (blue) to the second tube chamber → The two solvents mix slowly over time, the mixing is slowed by a fine sinter separating the two solvent chambers, to give crystals (orange) at solvent interface (green) over time

- Once single perfect crystals have been obtained, it is recommended that the crystals are kept in a sealed vessel with some of the liquid of crystallisation to prevent the crystal from 'drying out'. Single perfect crystals may contain solvent of crystallisation in the crystal lattice. Loss of this internal solvent from the crystals can result in the crystal lattice breaking down, and the crystals turning to powder.

Geology

In geology, solid-state recrystallization is a metamorphic process that occurs under situations of intense temperature and pressure where grains, atoms or molecules of a rock or mineral are packed closer together, creating a new crystal structure. The basic composition remains the same. This process can be illustrated by observing how snow recrystallizes to ice without melting.

As opposed to metasomatism, which is a chemical change caused by metamorphism, recrystallization is a physical process. However, recrystallization can occur when a local migration of chemicals results in the chemical change of the rock or mineral with no external addition of materials.

Limestone is a sedimentary rock that undergoes metamorphic recrystallization to form marble, and clays can recrystallize to muscovite mica.

Single crystal

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. The opposite of a single crystal sample is an amorphous structure where the atomic position is limited to short range order only. In between the two extremes exist *polycrystalline* and *paracrystalline* phases, which are made up of a number of smaller crystals known as *crystallites*. Because of a variety of entropic effects on the microstructure of solids, including the distorting effects of impurities and the mobility of crystallographic defects and dislocations, single crystals of meaningful size are exceedingly rare in nature, and can also be difficult to produce in the laboratory under controlled conditions.

A rod of semiconductor-grade polysilicon. (Held by Leo Rogers of Polycrystalline Silicon Technology Corporation (P.S.T.)

Because grain boundaries can have significant effects on the physical and electrical properties of a material, single crystals are of interest to industry, and have important industrial applications. The most notable of these is the use of single crystal silicon 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.

Fabrication of single crystals [as an example single crystalline silicon] usually involves the building of a crystal layer by layer of atoms. Techniques to produce large single crystals (boules) include slowly drawing a rotating "seed crystal" in a molten bath of feeder material [polycrystalline silicon](as in the Czochralski process and the Bridgeman technique). The feeder polycrystalline silicon is the purest material in the world. It is grown in rods and then melted for the formation of the single crystalline Czochralski and Bridgeman crystals.

An entirely different technology to create single crystalline materials is called epitaxy. This proces deposits micrometre layers of the same or different materials on the surface of an existing single crystal.

Uses

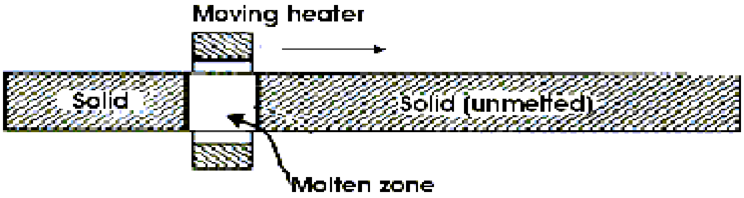
- Monocrystals of silicon and other semiconductors are important for manufacture of integrated circuits.

- Monocrystalline silicon photovoltaic cells have superior performance characteristics and higher price to chemically identical *polycrystalline* solar cells.
- 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.
- Monocrystals of metals, especially superalloys, are used for their special mechanical properties. Turbine blades of some gas turbines are made of single crystal cast superalloy.
- Monocrystals of copper (crystalline copper) are used for fine crystalline powders and hi tech wires.
- Monocrystaline superconductors have superior performance characteristics to chemically identical *polycrystaline* superconductors.
- The detailed study of the Crystal structure of a material by Bragg diffraction techniques is much easier with monocrystals. They may be grown for this purpose, even when the material is otherwise only needed in polycrystalline form.

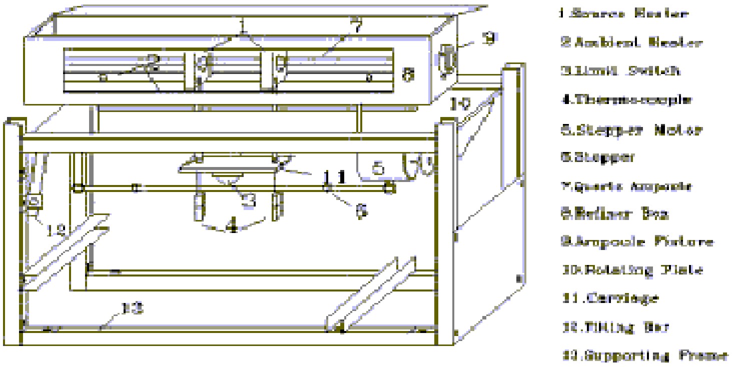
Purification

The growing interest in electronic and optical materials, has made this field one of the fastest growing areas of research. The preparation of semiconductors starts with the purification of the material down to impurity levels below 1 ppm (parts per million) and in some cases only ppt (parts per trillion) levels of impurity are allowed.

Typically, starting materials which may purchased from commercial vendors with nominal purity of 99.9999% or synthesized from pure elements. Zone-refining and vacuum sublimation are two standard processes to achieve this goal. Zone-refining was first introduced in 1952by Pfann, and has been successfully implemented to purify elements and compounds. The main principle is difference in solubility of an impurity in the liquid and solid phases of a material. The characteristic effect of zone-refining is to accumulate impurities at the ends of an ingot, thus leaving pure material in the central section. Vacuum sublimation is a routine method to purify starting materials from impurities having higher (under dynamic vacuum) or lower (closed tube) vapor pressures



Principle of zone refining: A moving heater melts a zone of the material that can accumulate impurities. The impurities are "swept" to the right end of the ingot. The heater is next moved fast to the left (without melting the material) and the process is repeated several times.



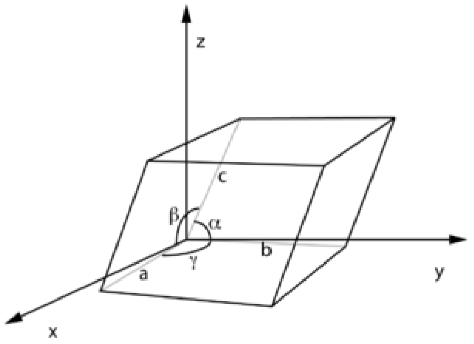
Schematics of a zone refiner containing two heaters for improved efficiency.

Crystal structure

In mineralogy and crystallography, a **crystal structure** is a unique arrangement of atoms in a crystal. A crystal structure is composed of a motif, a set of atoms arranged in a particular way, and a lattice. Motifs are located upon the points of a lattice, which is an array of points repeating periodically in three dimensions. The points can be thought of as forming identical tiny boxes, called unit cells, that fill the space of the lattice. The lengths of the edges of a unit cell and the angles between them are called the *lattice parameters*. The symmetry properties of the crystal are embodied in its space group. A crystal's structure and symmetry play a role in determining many of its properties, such as cleavage, electronic band structure, and optical properties.

Unit cell

The crystal structure of a material or the arrangement of atoms in a crystal structure can be described in terms of its unit cell. The unit cell is a tiny box containing one or more motifs, a spatial arrangement of atoms. The units cells stacked in three-dimensional space describes the bulk arrangement of atoms of the crystal. The unit cell is given by its lattice parameters, the length of the cell edges and the angles between them, while the positions of the atoms inside the unit cell are described by the set of atomic positions (x_i,y_i,z_i) measured from a lattice point. Although there are an infinite number of ways to specify a unit cell, for each crystal structure there is a *conventional unit cell,* which is chosen to display the *full symmetry* of the crystal (see below). However, the conventional unit cell is not always the smallest possible choice. A **primitive unit cell** of a particular crystal structure is the smallest possible volume one can construct with the arrangement of atoms in the crystal such that, when stacked, completely fills the space. This primitive unit cell will not always display all the symmetries inherent in the crystal. A Wigner-Seitz cell is a particular kind of primitive cell which has the same symmetry as the lattice. In a unit cell each atom has an identical environment when stacked in 3 dimensional space. In a primitive cell, each atom may not have the same environment.



Unit cell definition using parallelepiped with lengths a, b, c and angles between the sides given by α,β,γ

Classification of crystals by symmetry

The defining property of a crystal is its inherent symmetry, by which we mean that under certain *operations* the crystal remains unchanged. For example, rotating the crystal 180 degrees about a certain axis may result in an atomic configuration which is identical to the original configuration. The crystal is then said to have a twofold rotational symmetry about this axis. In addition to rotational symmetries like this, a crystal may have symmetries in the form of mirror planes and translational symmetries, and also the so-called *compound symmetries* which are a combination of translation and rotation/mirror symmetries. A full classification of a crystal is achieved when all of these inherent symmetries of the crystal are identified.

Crystal system

The crystal systems are a grouping of crystal structures according to the axial system used to describe their lattice.

Each crystal system consists of a set of three axes in a particular geometrical arrangement. There are seven unique crystal systems. The simplest and most symmetric, the cubic (or isometric) system, has the symmetry of a cube, that is, it exhibits four threefold rotational axes oriented at 109.5 degrees (the tetrahedral angle) with respect to each other. These threefold axes lie along the body diagonals of the cube. This definition of a cubic is correct, although many textbooks incorrectly state that a cube is defined by three mutually perpendicular axes of equal length – if this were true there would be far more than 14 Bravais lattices. The other six systems, in order of decreasing symmetry, are hexagonal, tetragonal, rhombohedral (also known as trigonal), orthorhombic, monoclinic and triclinic. Some crystallographers consider the hexagonal crystal system not to be its own crystal system, but instead a part of the trigonal crystal system. The crystal system and Bravais lattice of a crystal describe the (purely) translational symmetry of the crystal.

The Bravais lattices

When the crystal systems are combined with the various possible lattice centerings, we arrive at the Bravais lattices. They describe the geometric arrangement of the lattice points, and thereby the translational symmetry of the crystal. In three dimensions, there are 14 unique Bravais lattices which are distinct from one another in the translational symmetry they contain. All crystalline materials recognized until now (not including quasicrystals) fit in one of these arrangements. The fourteen three-dimensional lattices, classified by crystal system, are shown to the right. The Bravais lattices are sometimes referred to as *space lattices*.

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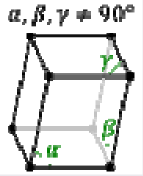
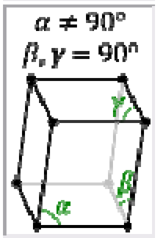
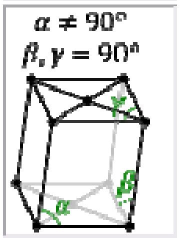
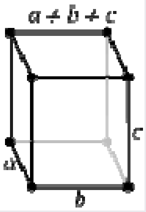
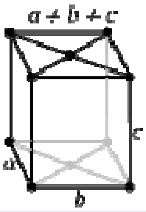
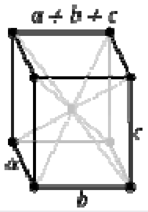
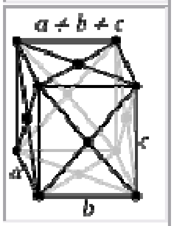
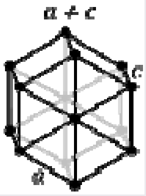
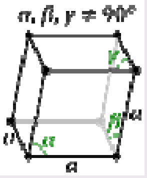
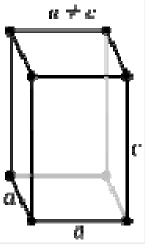
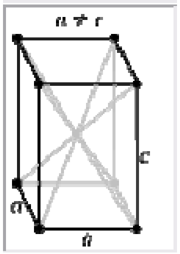
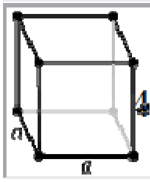
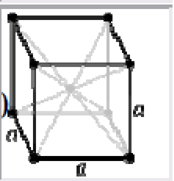
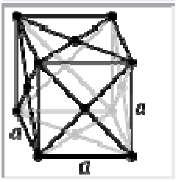
The crystal structure consists of the same group of atoms, the *basis*, positioned around each and every lattice point. This group of atoms therefore repeats indefinitely in three dimensions according to the arrangement of one of the 14 Bravais lattices. The characteristic rotation and mirror symmetries of the group of atoms, or unit cell, is described by its crystallographic point group.

The 7 Crystal systems (Defining Symmetry)	**The 14 Bravais Lattices:**			
triclinic (none)				
monoclinic (1 diad)	simple	base-centered		
				
orthorhombic (3 perpendicular diads)	simple	base-centered	body-centered	face-centered
				
hexagonal (1 hexad)				
rhombohedral (1 triad)				
tetragonal (1 tetrad)	simple	body-centered		
				
cubic (4 triads)	simple	body-centered	face-centered	
				

Point and space groups

The crystallographic point group or *crystal class* is the mathematical group comprising the symmetry operations that leave at least one point unmoved and that leave the appearance of the crystal structure unchanged. These symmetry operations can include *reflection*, which reflects the structure across a *reflection plane*, *rotation*, which rotates the structure a specified portion of a circle about a *rotation axis*, *inversion* which changes the sign of the coordinate of each point with respect to a *center of symmetry* or *inversion point* and *improper rotation*, which consists of a rotation about an axis followed by an inversion. Rotation axes (proper and improper), reflection planes, and centers of symmetry are collectively called *symmetry elements*. There are 32 possible crystal classes. Each one can be classified into one of the seven crystal systems.

The space group of the crystal structure is composed of the translational symmetry operations in addition to the operations of the point group. These include pure *translations* which move a point along a vector, *screw axes*, which rotate a point around an axis while translating parallel to the axis, and *glide planes*, which reflect a point through a plane while translating it parallel to the plane. There are 230 distinct space groups.

Physical properties

Defects or impurities in crystals

Real crystals feature defects or irregularities in the ideal arrangements described above and it is these defects that critically determine many of the electrical and mechanical properties of real materials. When one atom substitutes for one of the principal atomic components within the crystal structure, alteration in the electrical and thermal properties of the material may ensue. Impurities may also manifest as spin impurities in certain materials. Research on magnetic impurities demonstrates that substantial alteration of certain properties such as specific heat may be affected by small concentrations of an impurity, as for example impurities in semiconducting ferromagnetic alloys may lead to different properties as first predicted in the late 1960s. Dislocations in the crystal lattice allow shear at lower stress than that needed for a perfect crystal structure.

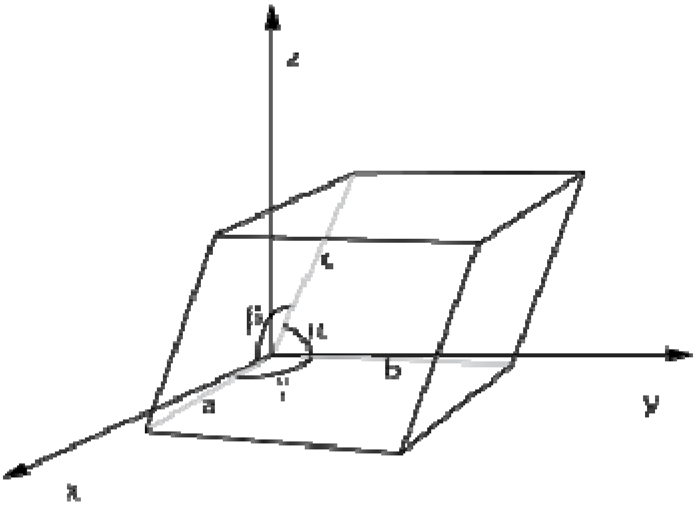
Crystal symmetry and physical properties

Twenty of the 32 crystal classes are so-called piezoelectric, and crystals belonging to one of these classes (point groups) display piezoelectricity. All 21 piezoelectric classes lack a center of symmetry. Any material develops a dielectric polarization when an electric field is applied, but a substance which has such a natural charge separation even in the absence of a field is called a polar material. Whether or not a material is polar is determined solely by its crystal structure. Only 10 of the 32 point groups are polar. All polar crystals are pyroelectric, so the 10 polar crystal classes are sometimes referred to as the pyroelectric classes.

There are a few crystal structures, notably the perovskite structure, which exhibit ferroelectric behavior. This is analogous to ferromagnetism, in that, in the absence of an electric field during production, the ferroelectric crystal does not exhibit a polarization. Upon the application of an electric field of sufficient magnitude, the crystal becomes permanently polarized. This polarization can be reversed by a sufficiently large counter-charge, in the same way that a ferromagnet can be reversed. However, it is important to note that, although they are called ferroelectrics, the effect is due to the crystal structure, not the presence of a ferrous metal. The angle between the normal to the two intersecting faces is called interfacial angle.

Incommensurate crystals have period-varying translational symmetry. The period between nodes of symmetry is constant in most crystals. The distance between nodes in an incommensurate crystal is dependent on the number of nodes between it and the base node.

Lattice constant



Unit cell definition using parallelepiped with lengths a, b, c and angles between the sides given by α,β,γ

The **Lattice Constant** refers to the constant distance between unit cells in a crystal lattice. Lattices in three dimensions generally have three lattice constants, referred to as *a*, *b*, and *c*. However, in the special case of cubic crystal structures, all of the constants are equal and we only refer to *a*. Similarly, in hexagonal crystal structures, the *a* and *b* constants are equal, and we only refer to the *a* and *c* constants. A group of lattice constants could be referred to as

lattice parameters. However, the full set of lattice parameters consist of the three lattice constants and the three angles between them.

For example the lattice constant for a common carbon diamond is *a = 3.57Å at 300 K*. It is important to note that the structure is equilateral although its actual shape can not be determined from only the lattice constant. Furthermore, in real applications, typically the average lattice constant is given. As lattice constants have the dimension of length, their SI unit is the meter. Lattice constants are typically on the order of several angstroms (i.e. tenths of a nanometre). Lattice constants can be determined techniques such as X-ray diffraction or with an atomic force microscope.

In epitaxial growth, the lattice constant is a measure of the structural compatibility between different materials. Lattice constant matching is important for growth of thin layers of materials on other materials; when the constants differ, strains are introduced into the layer, which prevents epitaxial growth of thicker layers without defects.

Lattice matching

Matching of lattice structures between two different semiconductor materials, allows forming of a region of band gap change in the material without introducing a change in crystal structure. It allows construction of advanced light-emitting diodes and diode lasers.

For example, gallium arsenide, aluminium gallium arsenide, and aluminium arsenide have almost equal lattice constants, making it possible to grow almost arbitrarily thick layers of one on the other one.

Lattice grading

Typically, films of different materials grown on the previous film or substrate are chosen to match the lattice constant of the prior layer to minimize film stress.

An alternative method is to grade the lattice constant from one value to another by a controlled altering the alloy ratio during film growth. The beginning of the grading layer will have a ratio to match the underlying lattice and the alloy at the end of the layer growth will match the desired final lattice for the following layer to be deposited.

The rate of change in alloy must be determined by the weighing of the penalty of layer strain and hence defect density vs. the cost of the time in the epitaxy tool.

For example, Indium gallium phosphide layers with a band-gap above 1.9 eV can be grown on Gallium Arsenide wafers with index grading.

Crystallography

Crystallography is the experimental science of determining the arrangement of atoms in solids. In older usage, it is the scientific study of crystals. The word "crystallography" is derived from the Greek words *crystallon* = cold drop / frozen drop, with its meaning extending to all solids with some degree of transparency, and *graphein* = write.

Before the development of X-ray diffraction crystallography (see below), the study of crystals was based on the geometry of the crystals. This involves measuring the angles of crystal faces relative to theoretical reference axes (crystallographic axes), and establishing the symmetry of the crystal in question. The former is carried out using a goniometer. The position in 3D space of each crystal face is plotted on a stereographic net, e.g. Wulff net or Lambert net. In fact, the pole to each face is plotted on the net. Each point is labelled with its Miller index. The final plot allows the symmetry of the crystal to be established.

Crystallographic methods now depend on the analysis of the diffraction patterns that emerge from a sample that is targeted by a beam of some type. The beam is not always electromagnetic radiation, even though X-rays are the most common choice. For some purposes electrons or neutrons are used, which is possible due to the wave properties of the particles. Crystallographers often explicitly state the type of illumination used when referring to a method, as with the terms **X-ray diffraction, neutron diffraction** and **electron diffraction.**

These three types of radiation interact with the specimen in different ways. X-rays interact with the spatial distribution of the valence electrons, while electrons are charged particles and therefore feel the total charge distribution of both the atomic nuclei and the surrounding electrons. Neutrons are scattered by the atomic nuclei through the strong nuclear forces, but in addition, the magnetic moment of neutrons is non-zero. They are therefore also scattered by magnetic fields. Because of these different forms of interaction, the three types of radiation are suitable for different crystallographic studies.

Theory

An image of a small object is usually generated by using a lens to focus the illuminating radiation, as is done with the rays of the visible spectrum in light microscopy. However, the wavelength of visible light (about 4000 to 7000 Angstroms) is three orders of magnitude longer then the length of typical atomic bonds and atoms themselves (about 1 to 2 Angstroms). Therefore, obtaining information about the spatial arrangement of atoms requires the use of radiation with shorter wavelengths, such as X-rays. Employing shorter wavelengths implied abandoning microscopy and true imaging, however, because there exists no material from which a lens capable of focusing this type of radiation can be created. (That said, scientists have had some success focusing X-rays with microscopic Fresnel zone plates made from gold, and by critical-angle reflection inside long tapered capillaries). Diffracted x-ray beams cannot be focussed to produce images, so the sample structure must be reconstructed from the diffraction pattern. Sharp features in the diffraction pattern arise from periodic, repeating structure in the sample, which are often very strong due to coherent reflection of many photons from many regularly spaced instances of similar structure, while non-periodic components of the structure result in diffuse (and usually weak) diffraction features.

Because of their highly ordered and repetitive structure, crystals give diffraction patterns of sharp Bragg reflection spots, and are ideal for analyzing the structure of solids.

Notation

See Miller index for a full treatment of this topic.

- Coordinates in *square brackets* such as **[100]** denote a direction vector (in real space).
- Coordinates in *angle brackets* or *chevrons* such as **<100>** denote a *family* of directions which are related by symmetry operations. In the cubic crystal system for example, **<100>** would mean [100], [010], [001] or the negative of any of those directions.
- Miller indices in *parentheses* such as **(100)** denote a plane of the crystal structure, and regular repetitions of that plane with a particular spacing. In the cubic system, the normal to the (hkl) plane is the direction [hkl], but in lower-symmetry cases, the normal to (hkl) is not parallel to [hkl].
- Indices in *curly brackets* or *braces* such as **{100}** denote a family of planes and their normals which are equivalent due to symmetry operations, much the way angle brackets denote a family of directions.