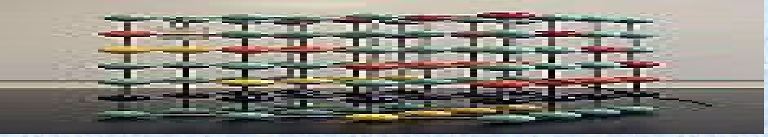
Adventures in Crystal Growth methods

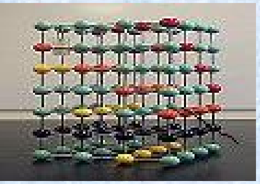


•INTRODUCTION TO CRYSTAL PHYSICS

- Matter exists in three states viz. solids, liquids and
- gases.
- All these states are composed of atoms and
- molecules.
- When we focus the solids, they are classified into
- many types based on several properties like
- electrical, mechanical, magnetic, optical, thermal
- etc.,.
- The main reason for these different properties of
- solids is their crystal structure.

- A **crystal** or **crystalline solid** is a solid material whose components (such as atoms, molecules or ions) are arranged in a highly ordered microscopic structure, forming a crystal lattice that extends in all directions

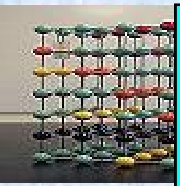
'*Crystal Physics*' or '*Crystallography*' is a branch of physics that deals with the study of all possible types of crystals and the physical properties of crystalline solids by the determination of their actual structure by using X-rays, neutron beams and electron beams.



•CLASSIFICATION OF SOLIDS

- Solids can broadly be classified into two types based on the
- arrangement of units of matter.
- The units of matter may be atoms, molecules or ions.
- They are,
  - Crystalline solids and
  - Non-crystalline (or) Amorphous solids

•CRYSTALLINE SOLIDS



- A substance is said to be crystalline when the
- arrangement of units of matter is regular and
- periodic.

- A crystalline material has directional properties and
- therefore called as anisotropic substance.

- A crystal has a sharp melting point.

- It possesses a regular shape and if it is broken, all
- broken pieces have the same regular shape.

•CRYSTALLINE SOLIDS

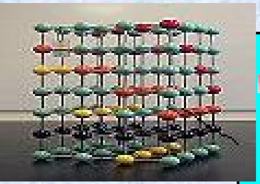
- A crystalline material can either be a single
- (mono) crystal or a polycrystal.

- A single crystal consists of only one crystal,
- whereas the polycrystalline material consists of
- many crystals separated by well-defined
- boundaries.

- Examples
- – Cu, Ag, Al, Mg etc,

•Carbon,Silicon,Germanium,

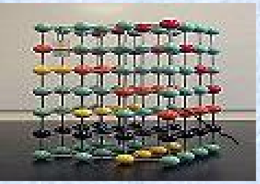
•NON CRYSTALLINE SOLIDS



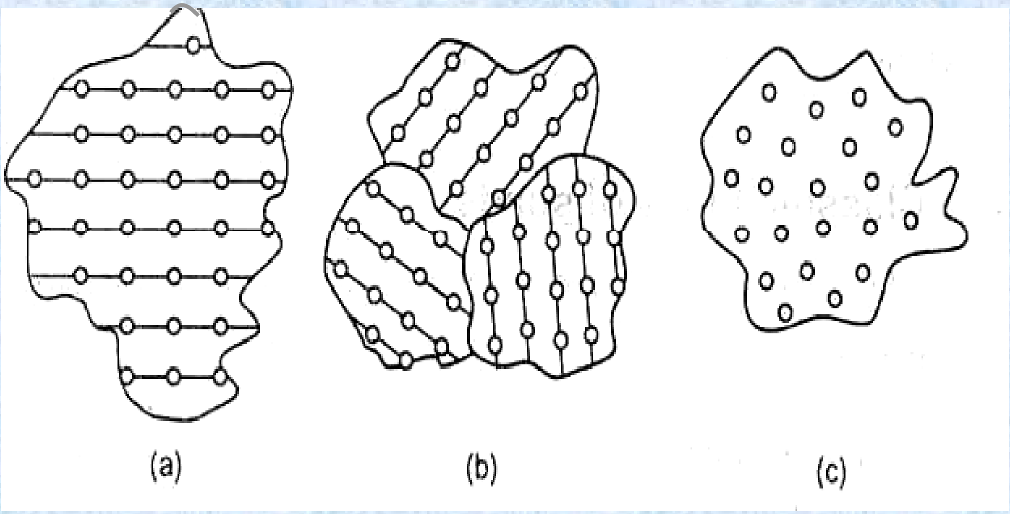
- In amorphous solids, the constituent particles
- are not arranged in an orderly manner. They
- are randomly distributed.

- They do not have directional properties and so
- they are called as `isotropic’ substances.

- They have wide range of melting point and do
- not possess a regular shape.
- Examples:
- Glass, Plastics, Rubber etc.,

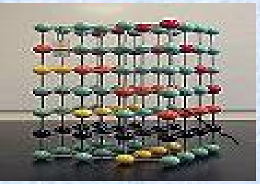


•ATOMIC ARRANGEMENT IN CRYSTALS



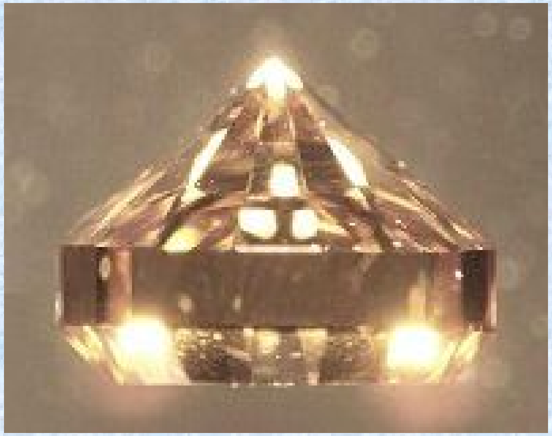
(a) mono (or) single crystals

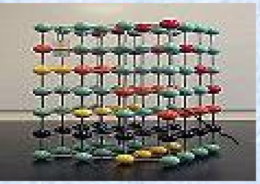
- (b) polycrystalline solids
- (c) amorphous solids



•CRYSTALS

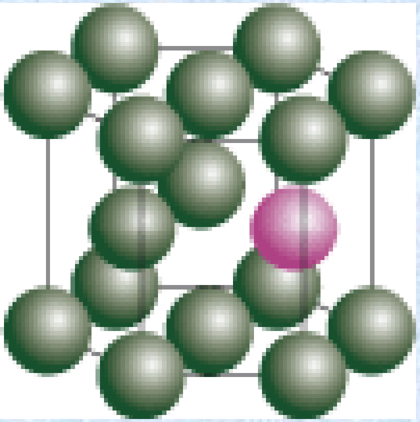
- It is a substance in which the fundamental particles are
- arranged in a systematic geometrical pattern.

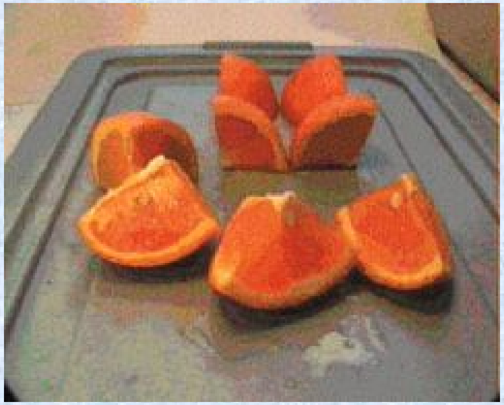


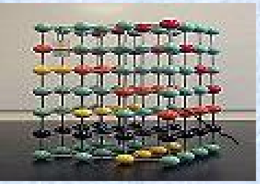


• UNIT CELL

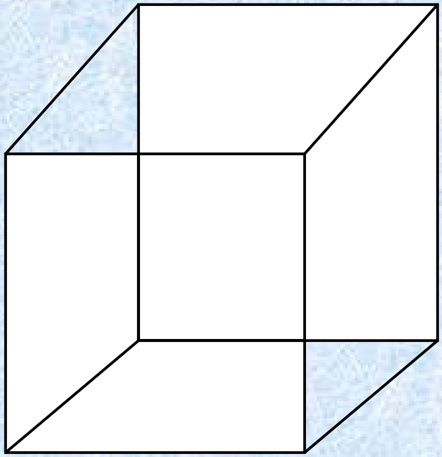
- A unit cell is defined as a fundamental building block
- of a crystal structure, which can generate the
- complete crystal by repeating its own dimensions in
- various directions.







• UNIT CELL



crystal growth methods

generally classified as:

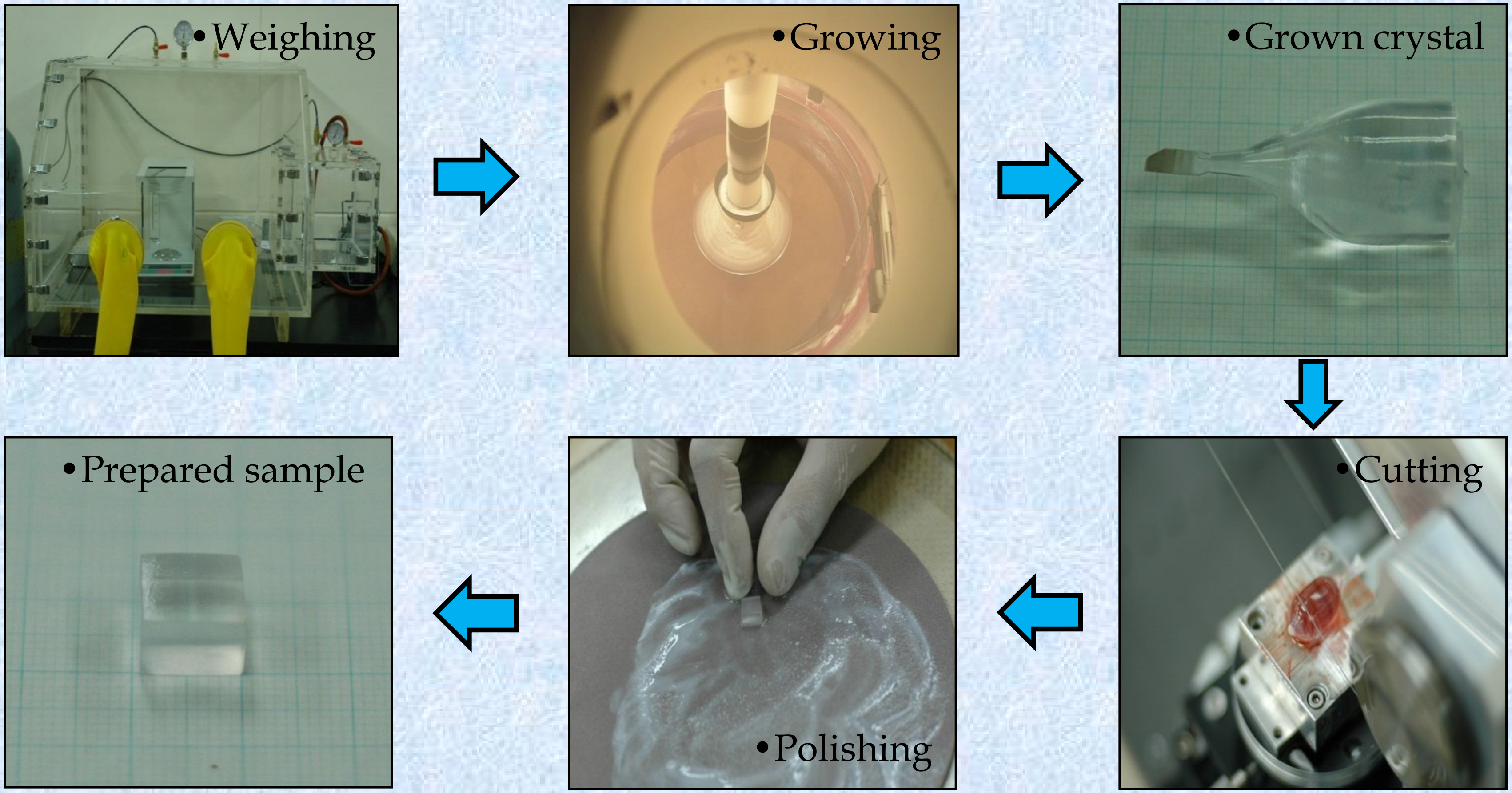
each method has several different versions

• melt growth	directional solidification from the melt ~ mm/hr
• solution growth	supersaturation ~ mm/day
• vapor growth	sublimation-condensation ~ µm/hr

Crystal Growth from Liquid (Melt)

- **Bridgman (“directional solidification”) ~1925’s**
- **Czochralski (“pulling”) ~1917’s**
- **Verneuil (“flame fusion”) ~early 1900’s**
- **Floating Zone (image furnace) ~1953’s**

Crystal grown process

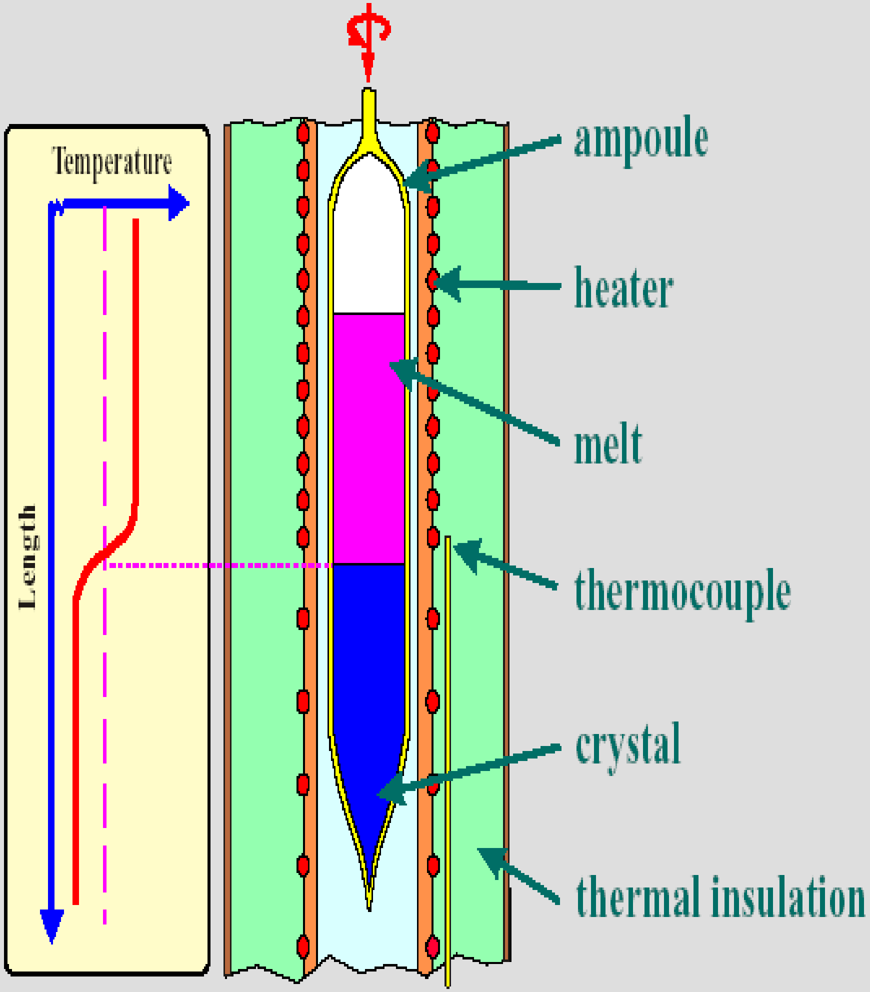


- Weighing
- Growing
- Grown crystal
- Cutting
- Polishing
- Prepared sample

Crystal grown process

- Weighing powder
- Putting powder into ampoule
- Sealing ampoule
- Measuring melting point
- Putting ampoule into furnace
- Starting grow crystal

The Bridgman-Stockbarger Method



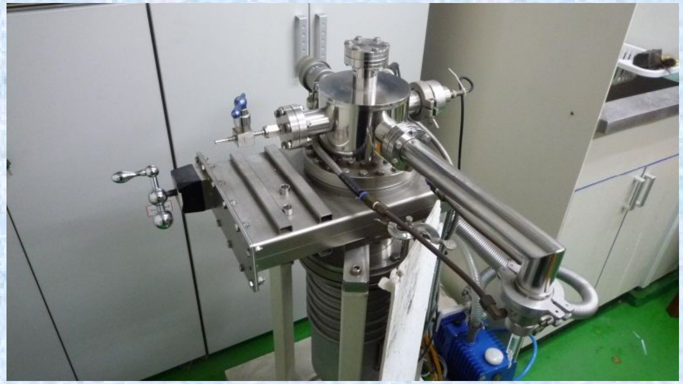
1. Sealing the starting materials in an ampoule
2. Melting
3. Crystal growth by passing the ampoule through the temperature gradient zone

Crystals grown:

As, Ag, LiI, SiAs, SnAs, $PrCl_3$, $LaCl_3$, $AgI_{0,3}Br_{0,7}$, $Ag_6Ge_{10}P_{12}$, $AuTe_2$, CsMnBr , $Cu_{12}Sb_4S_{13}$ etc.

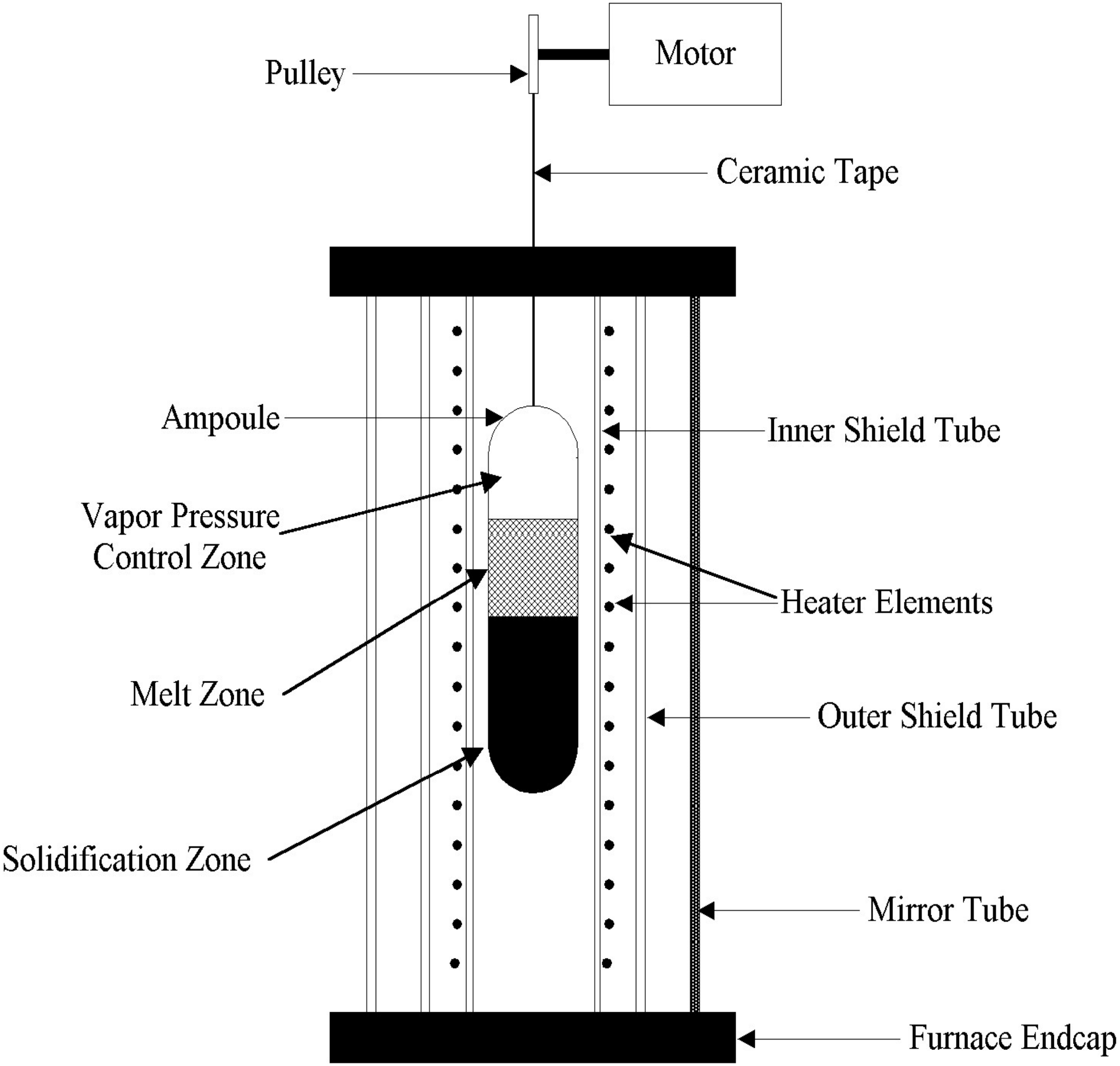
Bridgman Technique

- Two Bridgman system



- Vacuum machine

- Used to sealing ampoule

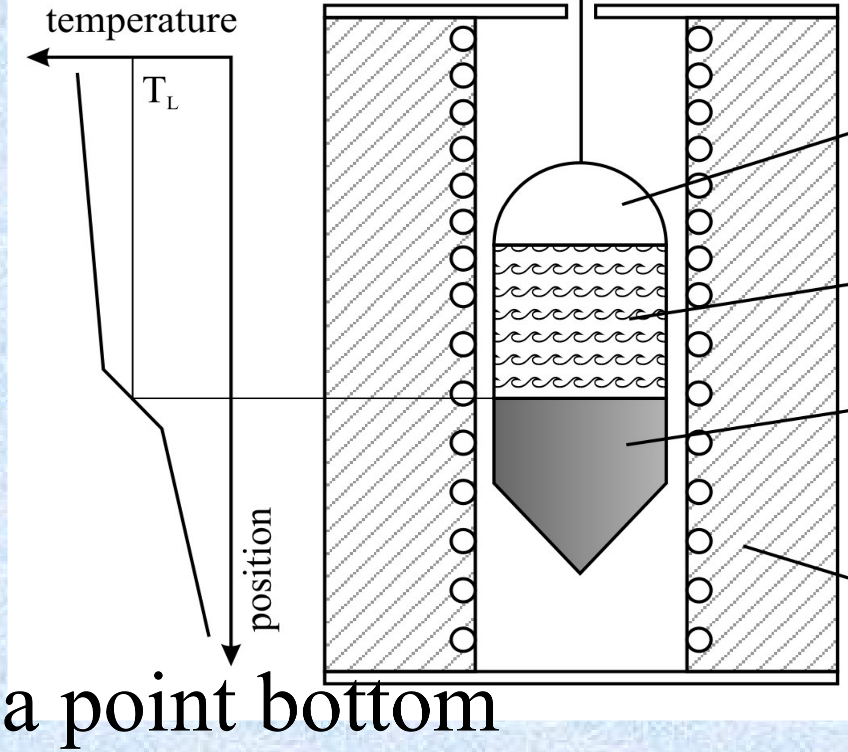

Motor
Pulley
Ceramic Tape
Ampoule
Inner Shield Tube
Vapor Pressure Control Zone
Heater Elements
Melt Zone
Outer Shield Tube
Solidification Zone
Mirror Tube
Furnace Endcap

- The Bridgman–Stockbarger technique is named after Harvard physicist Percy Williams Bridgman and physicist Donald C.Stockbarger (1895–1952).

The Bridgman technique is a method of growing single crystal ingot or boules. It is a popular method of producing certain semiconductor crystals, such as GaAs, II-V Crystals (ZnSe, CdS, CdSe)

The method involves heating polycrystalline material in a container above its melting point and slowly cooling it from one end where a seed crystal is located. Single crystal material is progressively formed along the length of the container. The process can be carried out in horizontal or vertical.

- **Bridgman method is based on a crystal growing from the melt, involves the relative displacement of melt and a temperature gradient furnace, fixed gradient and a moving melt/crystal**



- **Container selection**

- ❖ Tappered conically with a point bottom
- ❖ Should not contaminate crystals
- ❖ Should have lower thermal conductivity than crystal
- ❖ Free from corrosion
- ❖ Should have high melting point(quartz)

- Containor is lowered from hot to cold
- Rate of moment is abt .1-200 mm /hr

Or 1-30 mm/hr

- Crystal start to grow at the tip and from the first formed nucleus

advantages

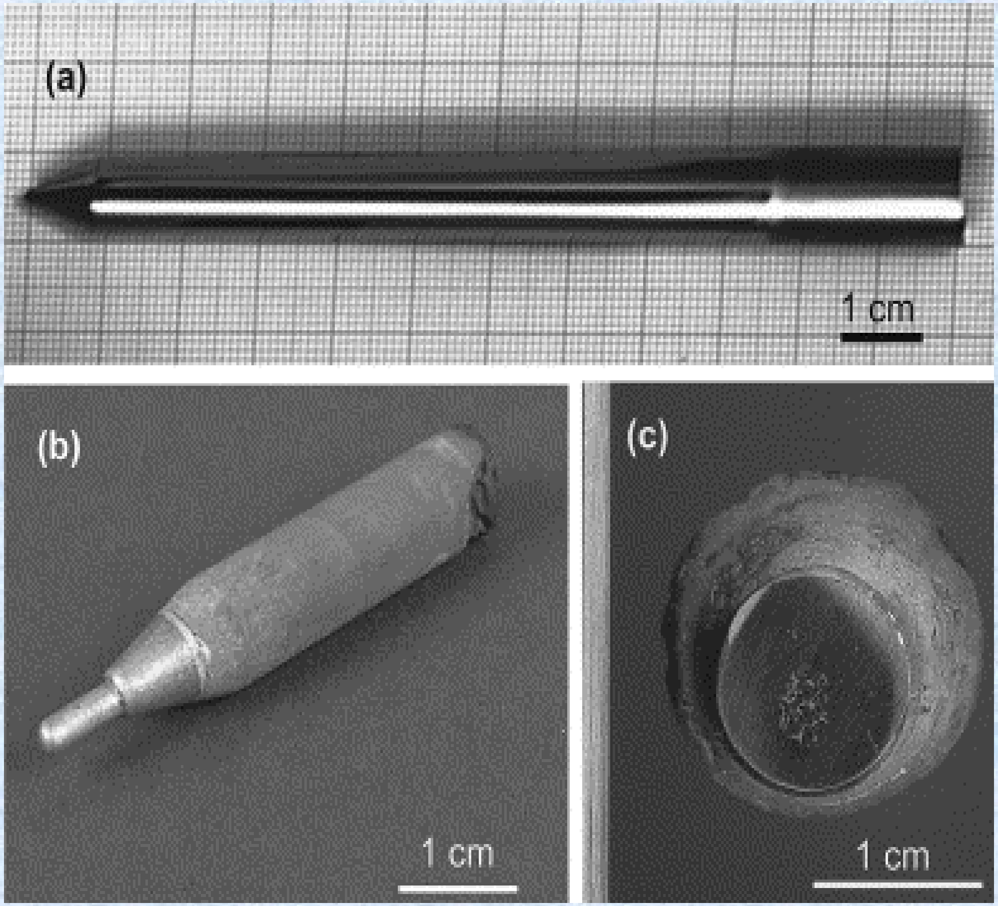
- the shape of the crystal is defined by the container
- no radial temperature gradients are needed to control the crystal shape.
- low thermal stresses result in low level of stress-induced dislocations.
- crystals may be grown in sealed ampules (easy control of stoichiometry)
- easy control and maintenance

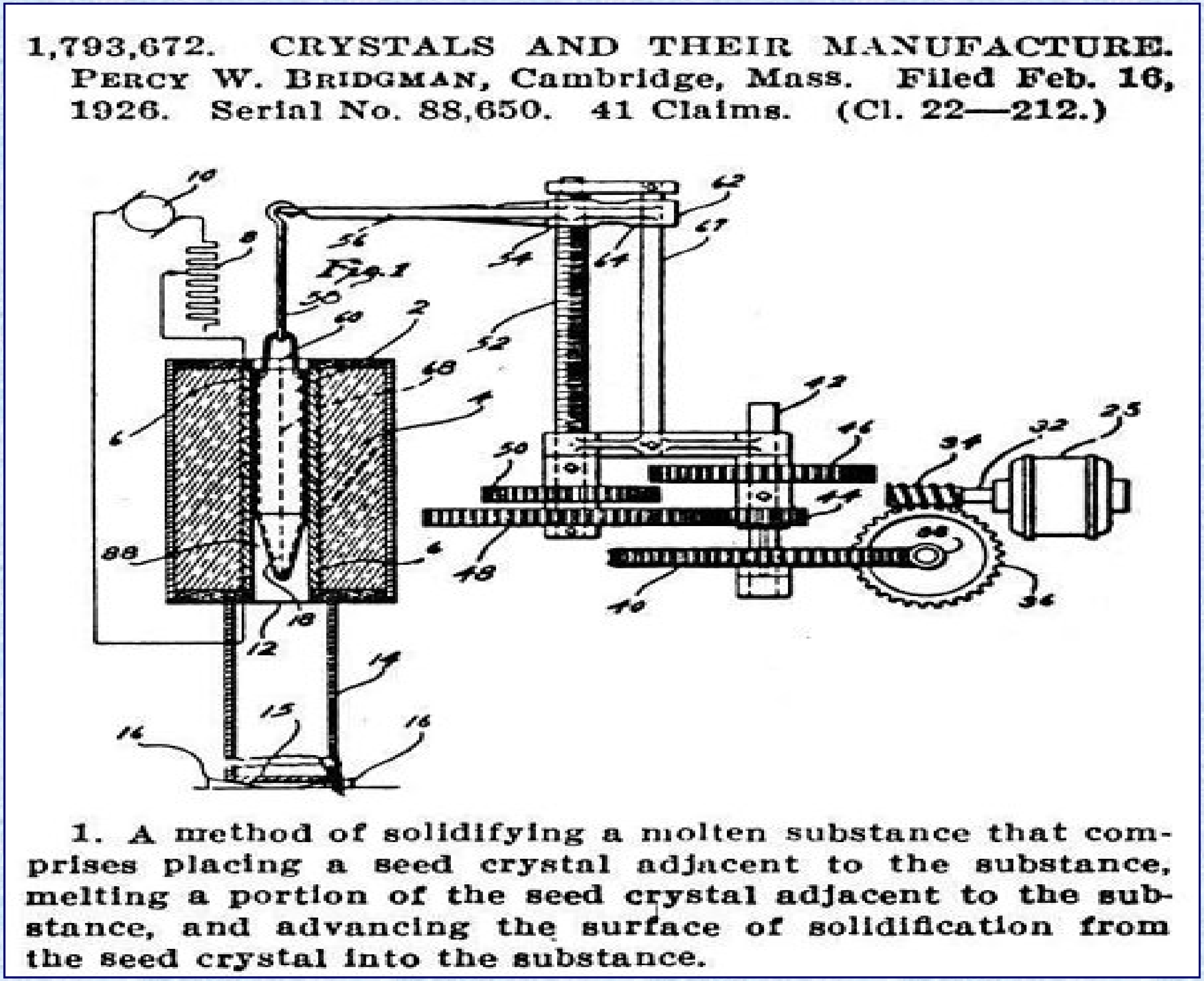
drawbacks

- confined growth (crucible may induce stresses during cooling)
- difficult to observe seeding and growing processes
- changes in natural convection as the melt is depleted
- delicate crucible and seed preparation, sealing, etc.

applications

- melts with volatile constituents:
  - III-V compounds (GaAs, lnP, GaSb)
  - II-VI compounds (CdTe)
- ternary compounds:
  - $\mathrm{Ga_{1-x}ln_xAs}$, $\mathrm{Ga_{1-x}ln_xSb}$, $\mathrm{Hg_{1-x}Cd_xTe}$


(a)
1 cm
(b)
1 cm
(c)
1 cm

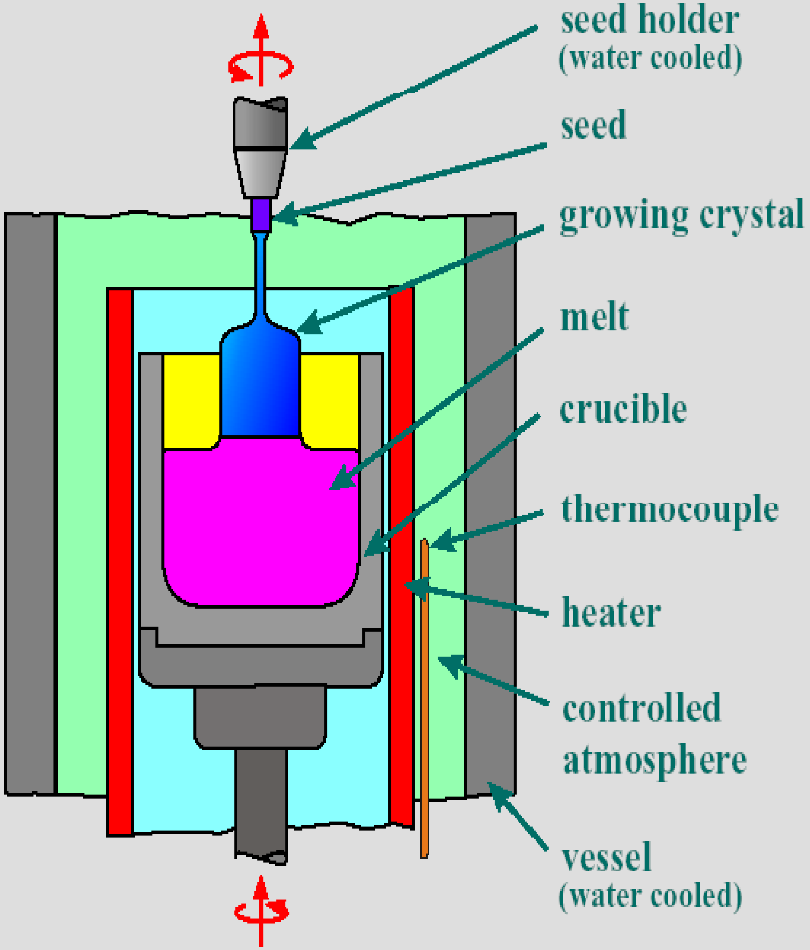


1,793,672. CRYSTALS AND THEIR MANUFACTURE. Percy W. Bridgman, Cambridge, Mass. Filed Feb. 16, 1926. Serial No. 88,650. 41 Claims. (Cl. 22—212.)

1. A method of solidifying a molten substance that comprises placing a seed crystal adjacent to the substance, melting a portion of the seed crystal adjacent to the substance, and advancing the surface of solidification from the seed crystal into the substance.

Czochralski method

The Czochralski method

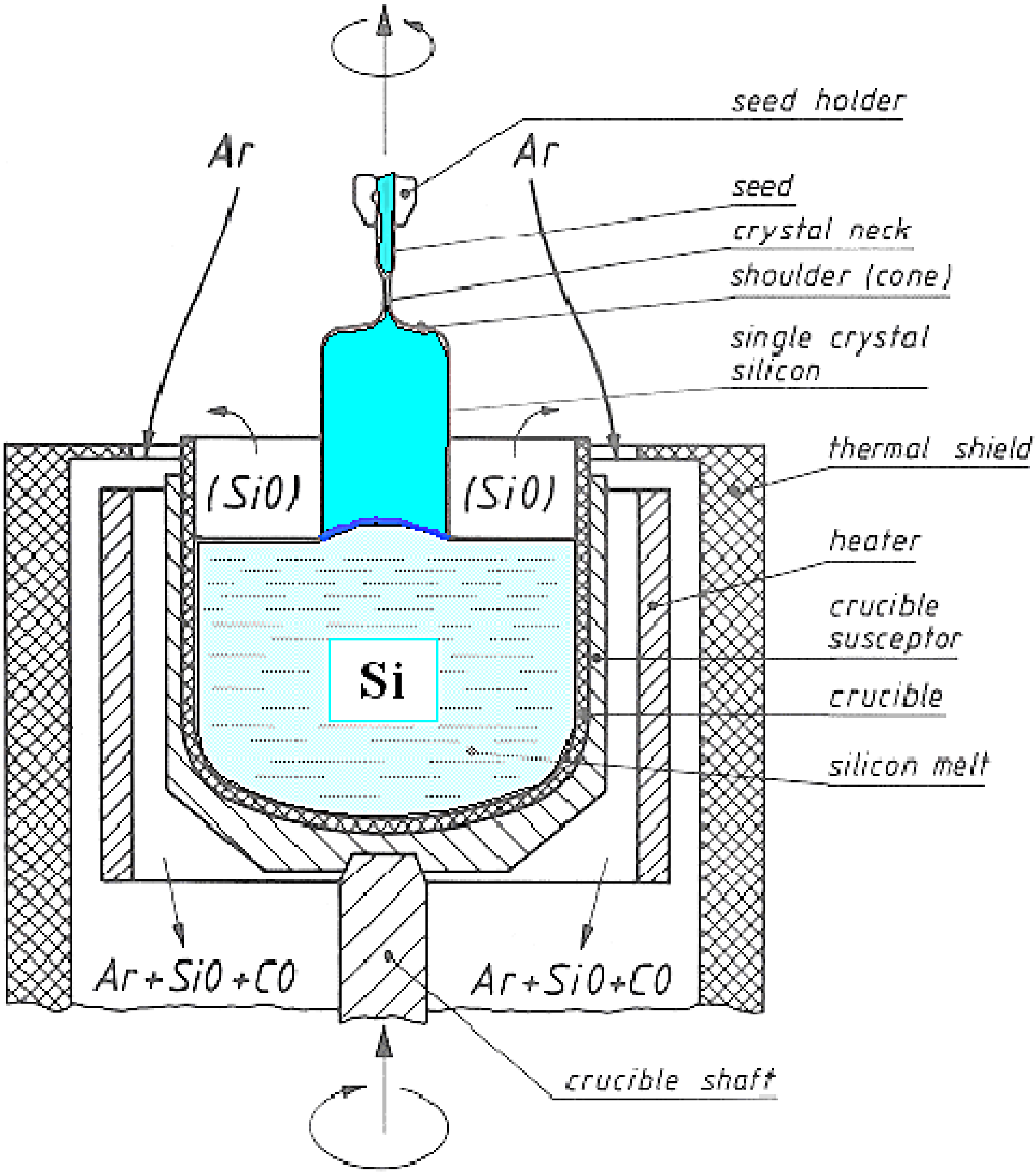


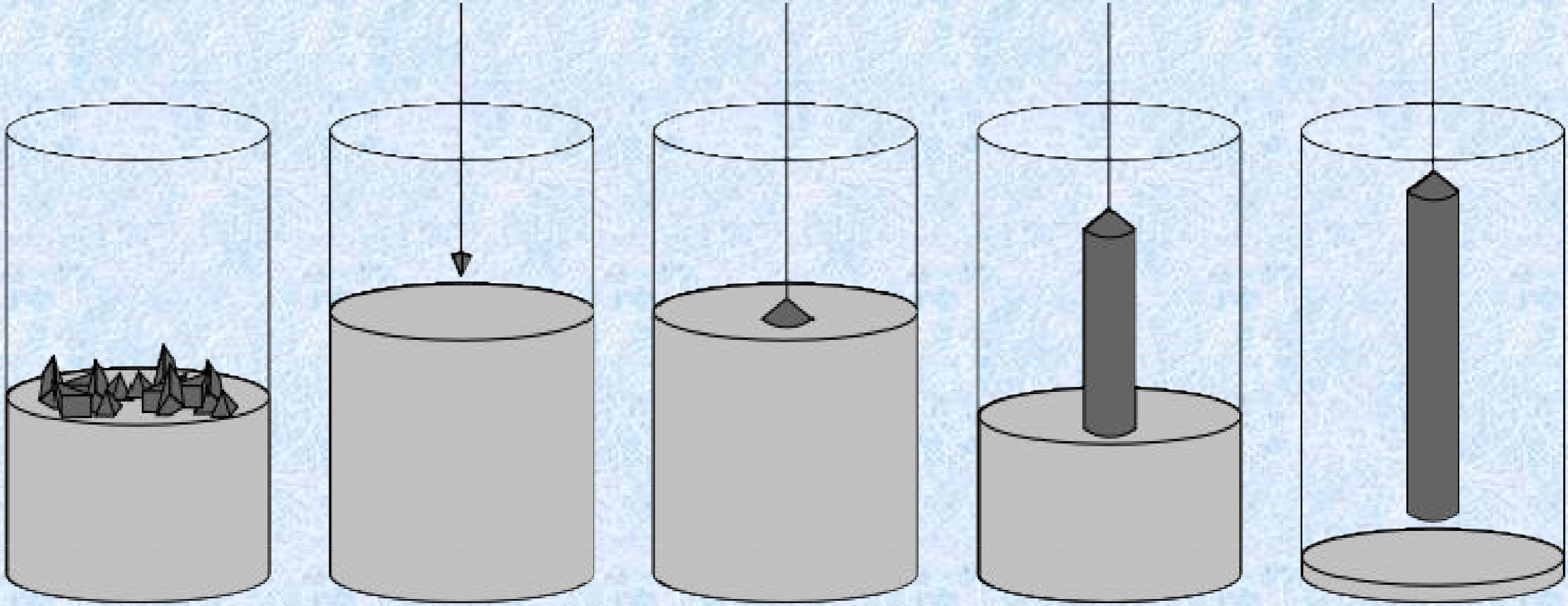
1. Melting of the starting material
2. Seeding
3. Necking
4. Shouldering
5. Equal diameter growth

Crystals grown:

Si, Ge, Sn, Bi, Au, AlSb, InSb, GaSb, CsJ, Kbr, CaF_2, BaF_2, NaCl, Li_3N, Al-Pd-Mn etc.

Beginning of crystal growth





Melting of polysilicon, doping

Introduction of the seed crystal

Beginning of the crystal growth

Crystal pulling

Formed crystal with a residue of melted silicon

The **Czochralski process** is a method of crystal growth used to obtain single crystals of semiconductors (e.g.Si,Ge and Ga As), metals (e.g.palladium,platinum,silver,gold), salts, and synthetic gemstones. The process is named after Polish scientist Jan Czochralski, who discovered the method in 1916 while investigating the crystallization rates of metals.

The most important application may be the growth of large cylindrical ingots, or boules, of single crystal silicon. Other semiconductors, such as Ga As, can also be grown by this method, although lower defect than Bridgman method.

CZOCHRALSKI METHOD

- **Interesting crystal pulling technique (but can you pronounce and spell the name!)**
- **Single crystal growth from the melt precursor(s)**
- **Crystal seed of material to be grown placed in contact with surface of melt**
- **Temperature of melt held just above melting point**
- **Seed gradually pulled out of the melt (not with your hands of course, special crystal pulling equipment is used)**

CZOCHRALSKI METHOD

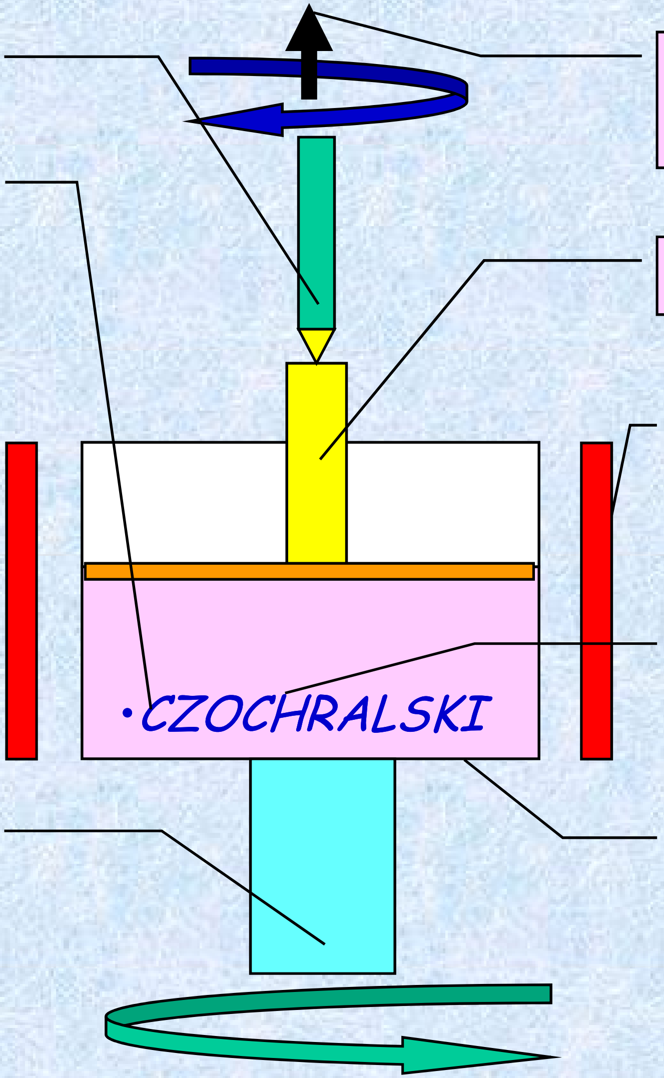
- **Melt solidifies on surface of seed**
- **Melt and seed usually rotated counterclockwise with respect to each other to maintain constant temperature and to facilitate uniformity of the melt during crystal growth, produces higher quality crystals, less defects**
- **Inert atmosphere, often under pressure around growing crystal and melt to prevent any materials loss and undesirable reactions like oxidation..etc**

- *Crystal seed*

- *Inert atmosphere* under pressure prevents material loss and unwanted reactions

- *Layer of molten oxide* like B_2O_3 prevents preferential volatilization of one

- *Counterclockwise rotation of melt and crystal being pulled from melt, helps maintain uniform T, composition and homogeneity of crystal growth*



- Pulling direction of seed on rod

- Growing crystal

- Heater

- Melt just above mp

- High viscosity low vapor pressure

Czochralski-Kyropoulos (2)

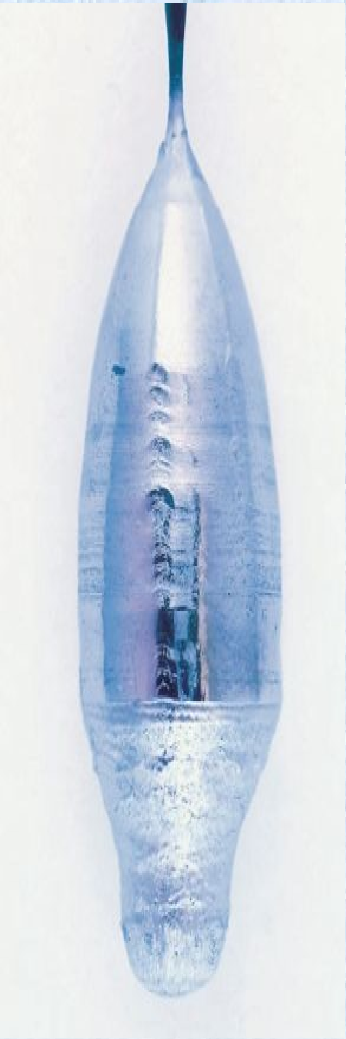
advantages

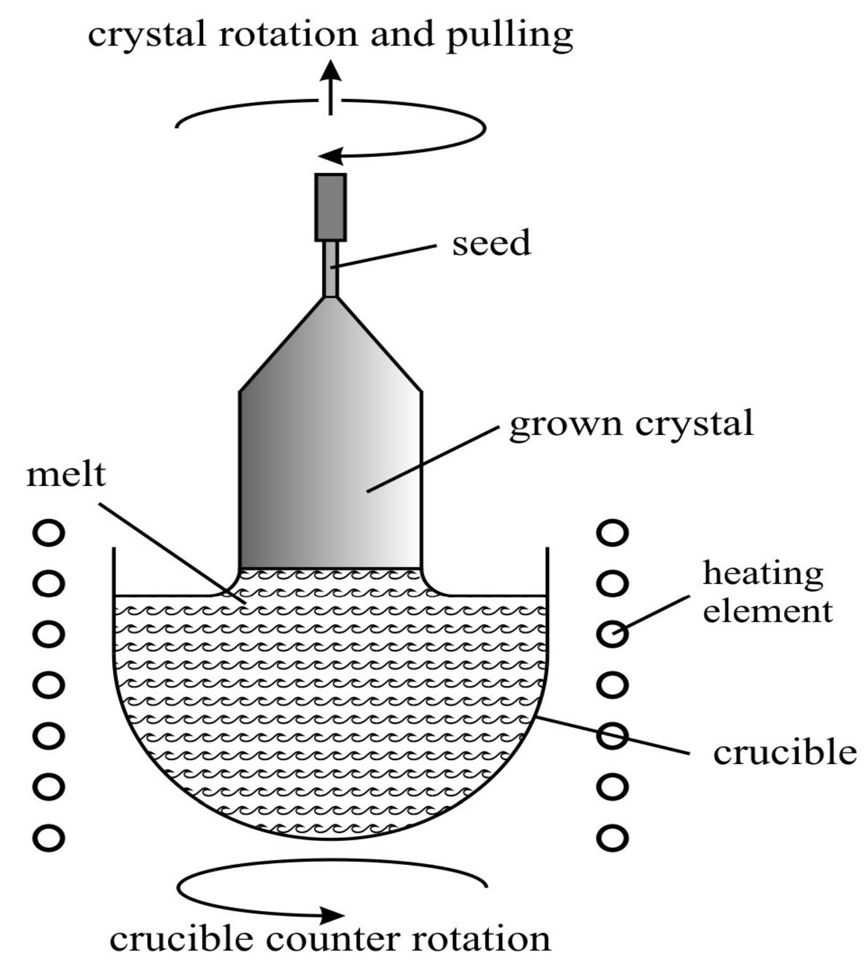
- growth from free surface (stress free)
- crystal can be observed during the growth process
- forced convection easy to impose
- large crystals can be obtained
- high crystalline perfection can be achieved
- good radial homogeneity

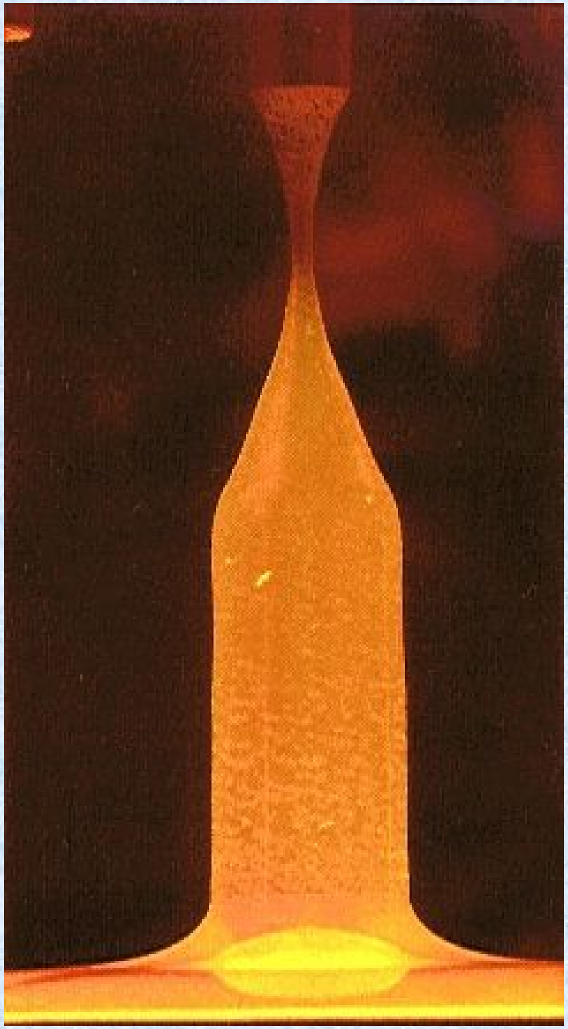
drawbacks

- delicate start (seeding, necking) and sophisticated further control
- delicate mechanics (the crystal has to be rotated; rotation of the crucible is desirable)
- batch process (limited productivity)

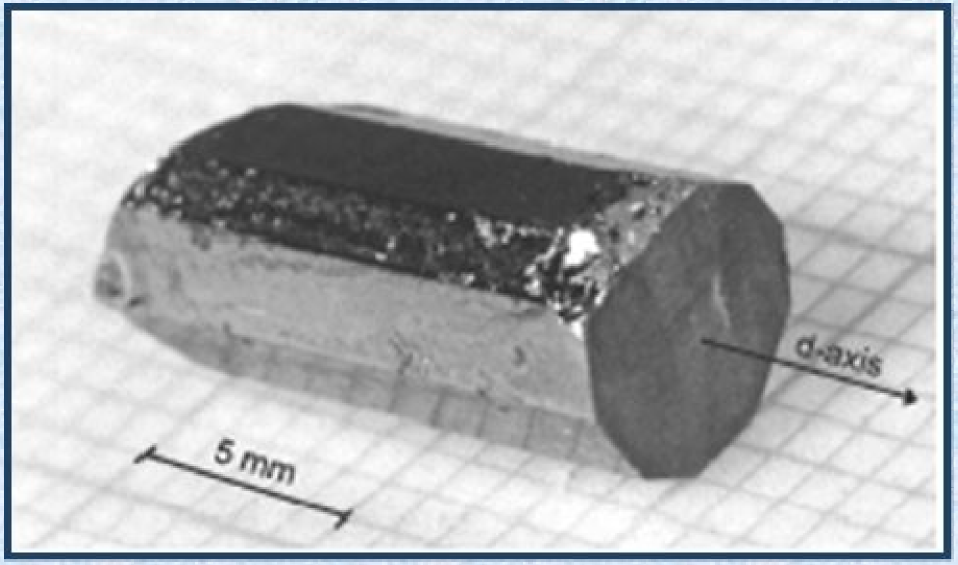
•Czochralski method







- Czochralski method



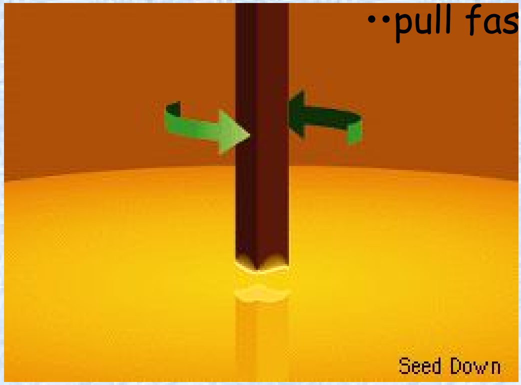
- Al-Co-Ni decagonal QC

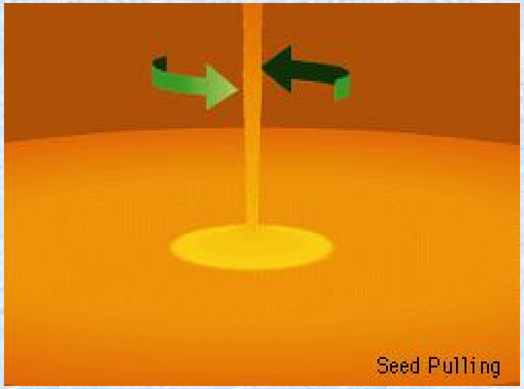
•Czochralski Growth

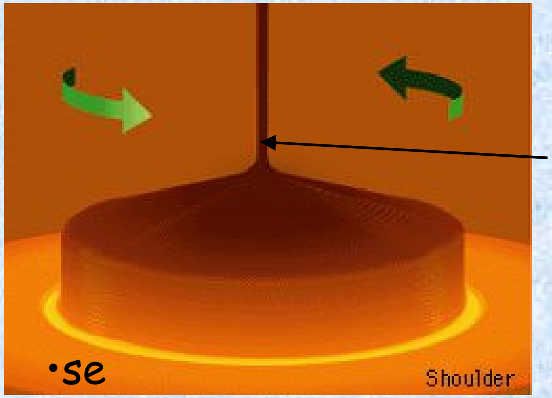
- •Load EGS+Impurities P, B, As
- •pump-out, •seed down,
- •pull fast, •pull slow

•EG
S

•100 kg







•se
ed

•Neck confines

•dislocations

•Crystal solidifies

Φ increases -

pull rate decreases

•(Photo courtesy of Ruth Carranza.))

•(More information on crystal growth at

•http://www.memc.com/co-as-description-crystal-growth.asp

•Also, see animations of http://www.memc.com/co-as-process-animation.asp)

EXAMPLES OF CZOCHRALSKI GROWN SCs

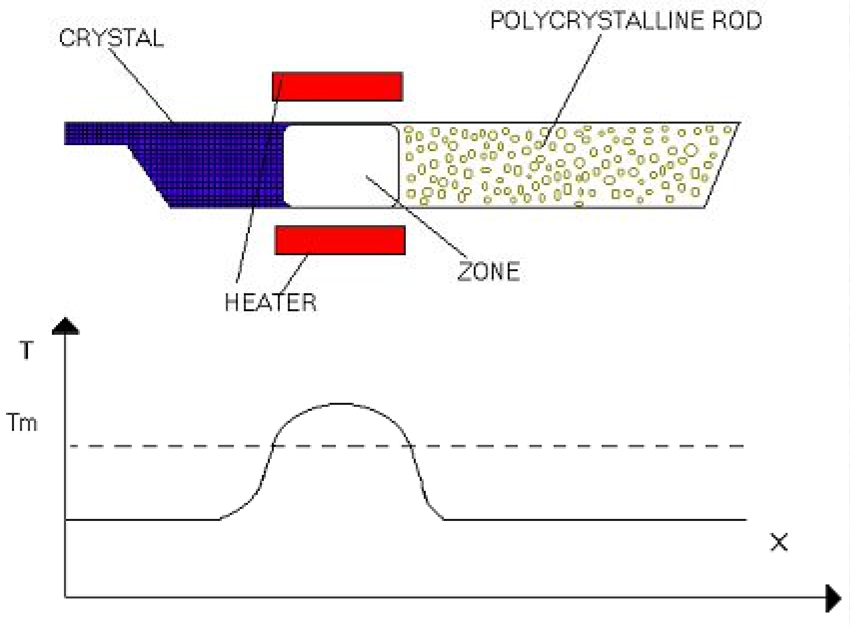
- **superconducting films**
- ***GaAlInP*** **- alloy semiconductor -** ***near IR diode lasers***
- ***GaAs*** **wafers –** ***red laser diodes*** **-** ***photonic crystal devices***
- $Nd_xY_{3-x}Al_5O_{12}$ **– neodynium YAG -** ***NIR solid state lasers*** **- 1.06 microns**

ZONE-MELTING

- This method was discovered by Pfann at 1952
- Capable to produce variety of organic and inorganic vrystals of extream high purity
- Till now silicon produced by this method offers the best quality crystals

zone melting (1)


ultra-pure silicon



characteristics:

- only a small part of the charge is molten
- material is added to molten region
- molten zone is advanced by moving the charge or the gradient
- axial temperature gradient is imposed along the crucible

ZONE MELTING CRYSTAL GROWTH AND PURIFICATION OF SOLIDS

- **Method related to the Stockbarger technique - *thermal profile furnace employed* - material contained in a boat**
- **Only a small region of the charge is melted at any one time - initially part of the melt is in contact with the seed**
- ***Boat containing sample pulled at a controlled velocity through the thermal profile furnace***
- ***Zone of material melted*, hence the name of the method - oriented solidification of crystal occurs on the seed - simultaneously more of the charge melts**

ZONE MELTING CRYSTAL GROWTH AND PURIFICATION OF SOLIDS

- *Partitioning of impurities occurs between melt and crystal*
- **Basis of the zone refining methods for purifying solids**
- **Impurities concentrate in melt more than the solid phase** ***where structure-energy constraints of crystal sites more severe than melt*** **- impurities swept out of crystal by moving the liquid zone**
- **Used for** ***purifying materials like W, Si, Ge, Au, Pt to ppb*** **level of impurities, often required for device applications**

zone melting (2)

advantages

Charge is purified by repeated passage of the zone (zone refining).

Crystals may be grown in sealed ampules or without containers (floating zone).

Steady-state growth possible.

Zone leveling is possible; can lead to superior axial homogeneity.

Simple: no need to control the shape of the crystal.

Radial temperature gradients are high.

drawbacks

Hard to observe the seeding process and the growing crystal.

In floating zone, materials with high vapor pressure can not be grown.

•Float Zone Method for Crystal Growth

- • An alternative process is the float
- zone process which can be used for
- refining or single crystal growth.

•No crucible - no impurities

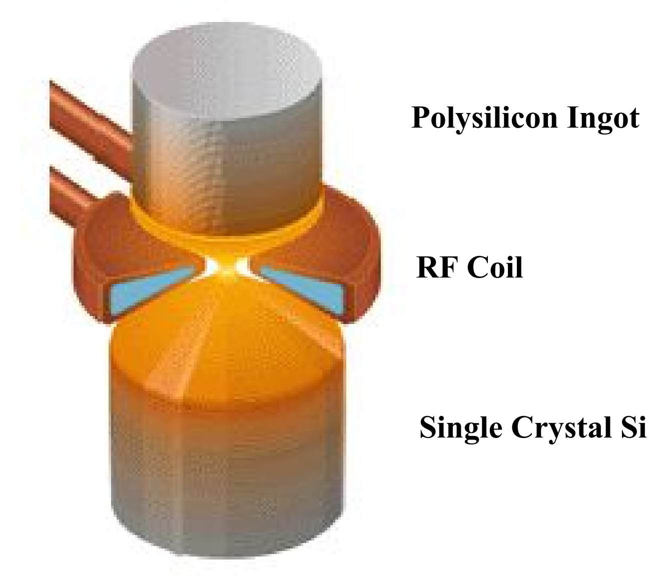


Figure 3–7 Basic Float-Zone (FZ) crystal growth or zone refining apparatus. This figure was taken directly from the Silicon Database on the Mitsubishi Materials Silicon Corporation web site at www.egg.or.jp/MSIL/english/index-e.html.

•EGS

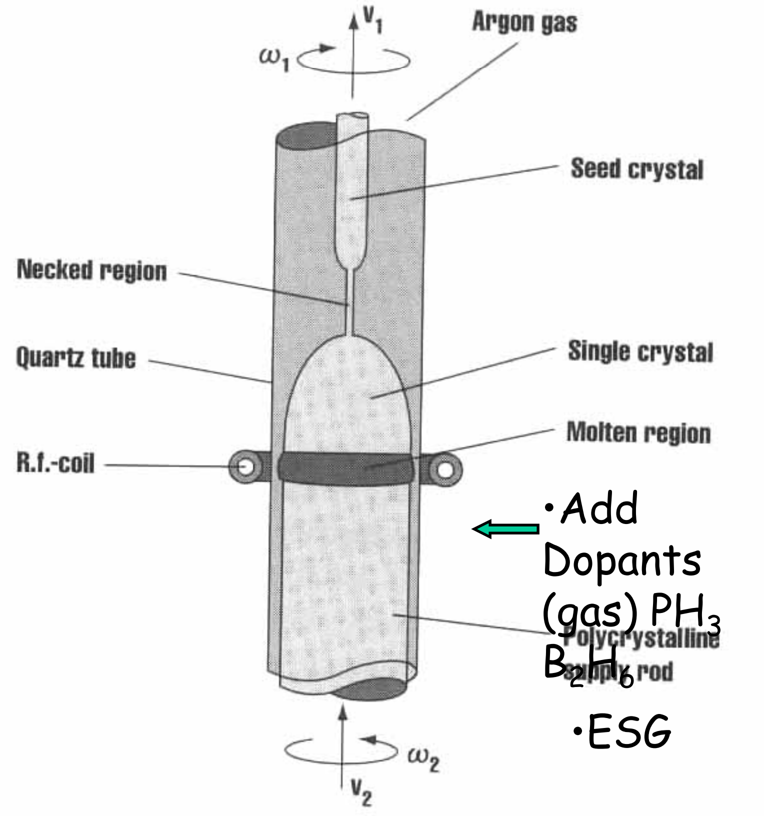
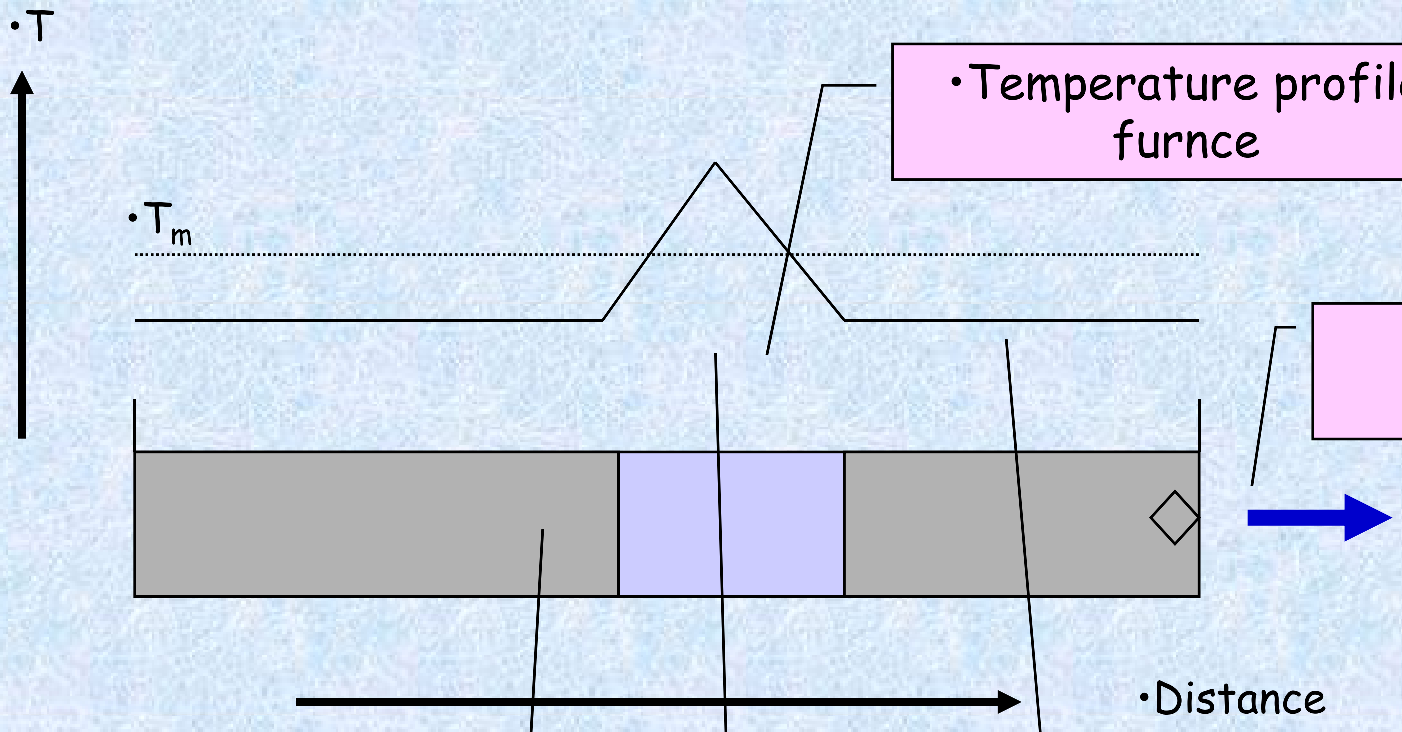


Figure 2-21 Schematic of a float zone refining system.

•Add Dopants (gas) PH_3 B_2H_6

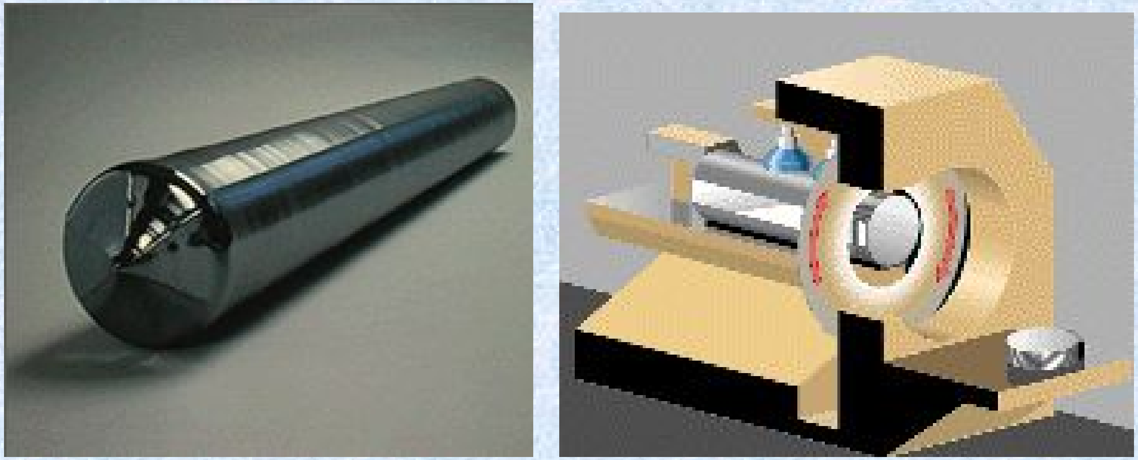
•ESG

•ZONE MELTING CRYSTAL GROWTH AND PURIFICATION OF SOLIDS



- Temperature profile furnce
- Pulling direction
- Crystal or powder
- Crystal growing from seed
- Localized melt region - impurities concentrated in melt – energetic benefit

•Crystal Growth and Wafers Fabrication



- • **After crystal pulling, the**
- **boule is shaped and cut into**
- **wafers which are then**
- **polished on one side.**

•(See animations of crystal polishing etc. at

• http://www.memc.com/co-as-process-animation.asp)

FROM INGOT TO FINISHED WAFER: SLICING, ETCHING, and POLISHING

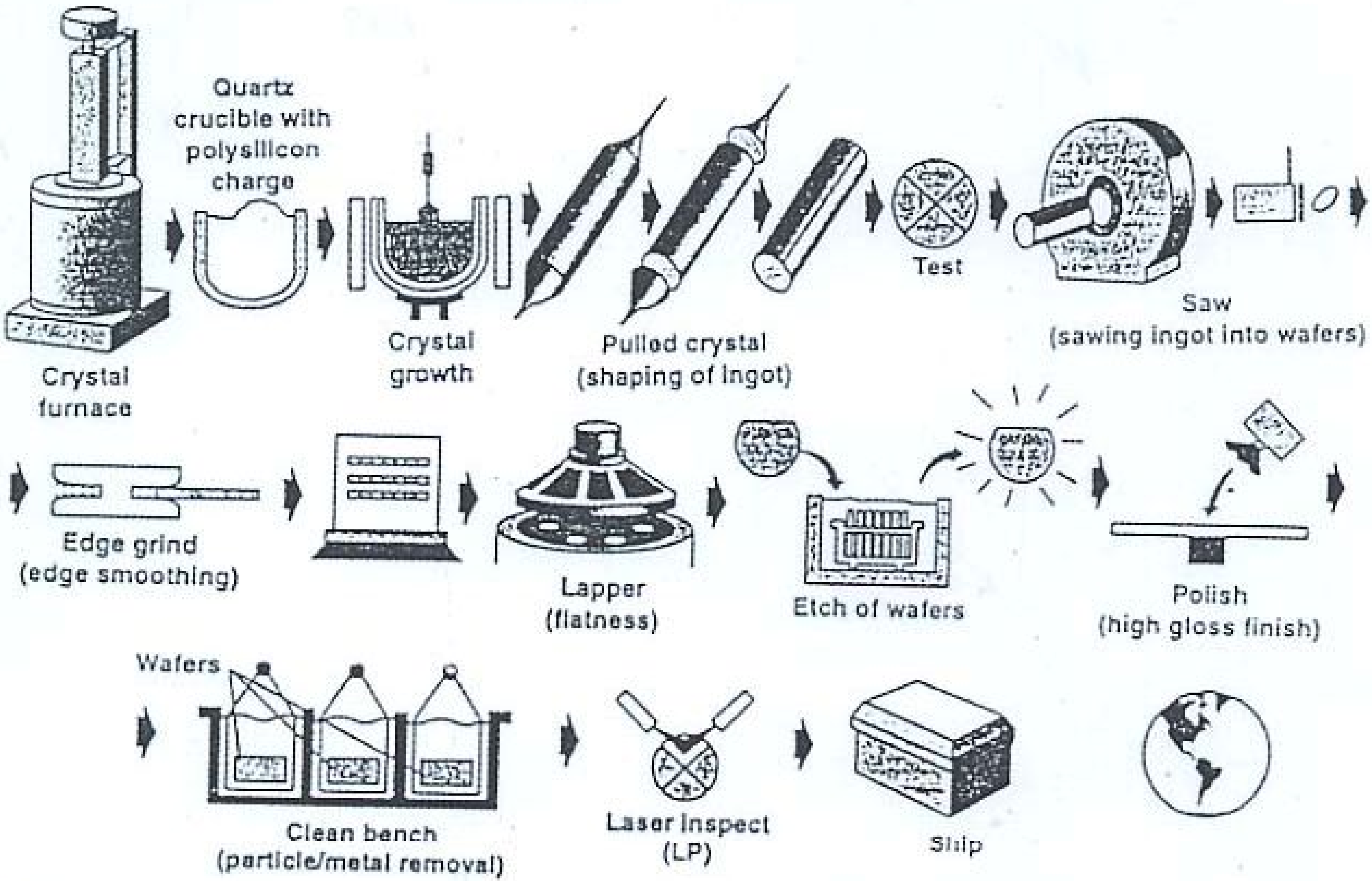


Fig. 1-16 Steps in the wafering process.

•http://www.memc.com/co-as-process-animation.asp •After Wolf&Tauber

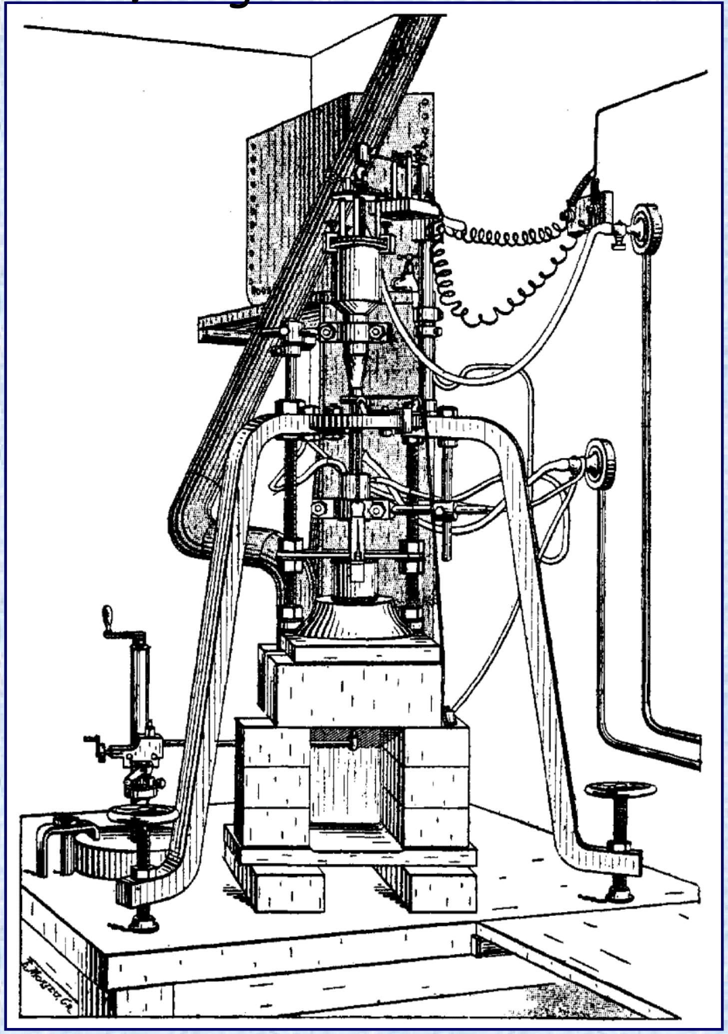
Verneuil method

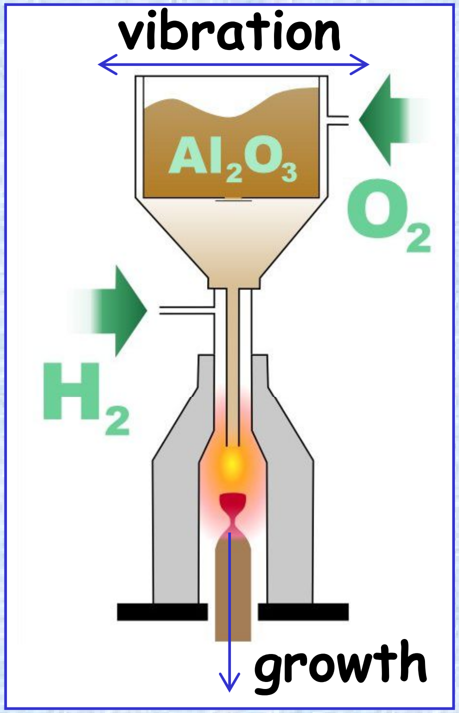
The **Verneuil process**, also called **flame fusion**, is a method of manufacturing synthetic gemstones, developed in 1902 by the French chemist Auguste Verneuil. It is primarily used to produce the ruby and sapphire varieties of corundum, as well as the diamond simulants rutile and strontium titanate.

- The principle of the process involves melting a finely powdered substance using an oxyhdrogen flame, and crystallising the melted droplets into a boule. The process is considered to be the founding step of modern industrial crystal growth technology, and remains in wide use to this day.

Verneuil

1902, Auguste Verneuil

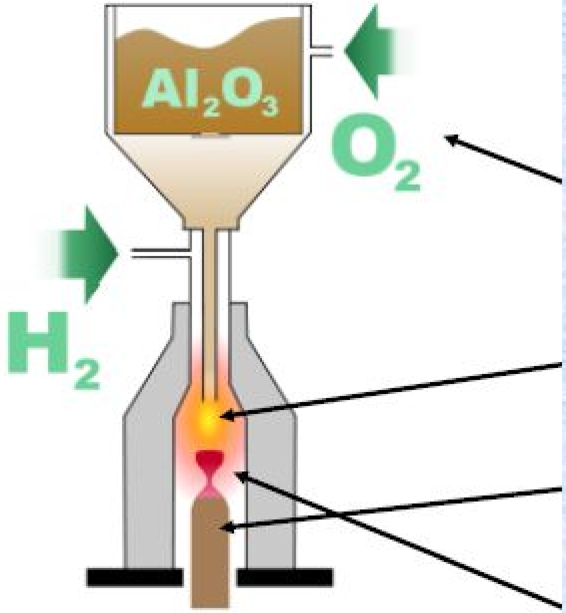




characteristics:

- no crucible contamination
- highly pure starting material (>99.9995%)
- strict control of flame temperature
- precise positioning of melted region

Verneuil Process



- First used ~1902-1910 for large-scale
  sapphire / ruby growth (Al_2O_3)

O_2 + Al_2O_3 inlet

O_2 + H_2 mix and ignite, T > 2000K

Molten drops fall onto “pedestal”

xtal forms & grows

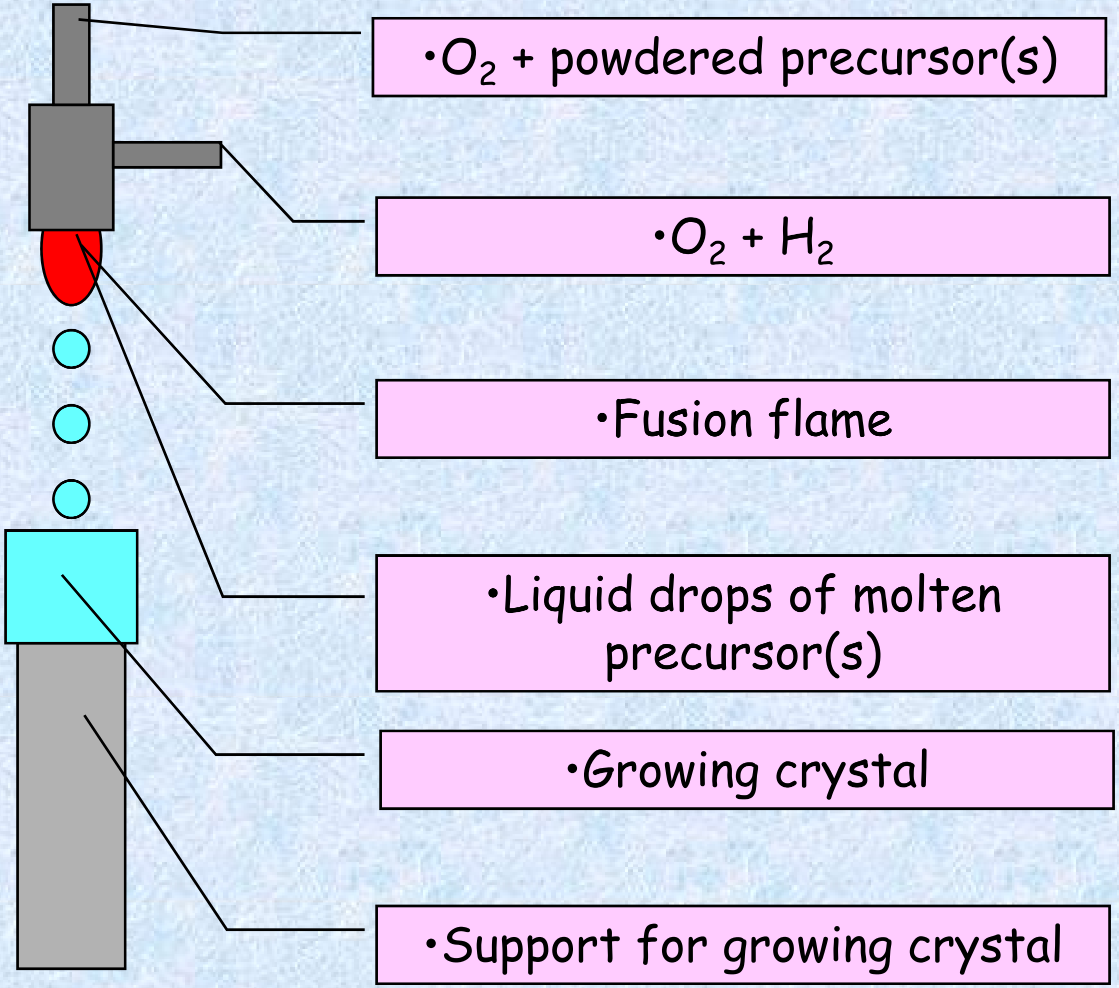
Example of Al_2O_3 xtal (right end)

VERNEUIL FUSION FLAME METHOD

- **1904 first recorded use of the method, *useful for growing crystals of extremely high melting and refractory metal oxides*, examples include:**
- **Ruby red from Cr^{3+}/Al_2O_3 powder, sapphire blue from Cr_2^{6+}/Al_2O_3 powder, luminescent host CaO powder**
- **Starting material fine powder form, passed through O_2/H_2 flame or plasma torch**
- **Melting of the powder occurs in the flame, molten microdroplets fall onto the surface of a seed or growing crystal, leads to controlled crystal growth**

- The process was designed primarily for the synthesis of rubies, which became the first gemstones to be synthetically produced
- One of the most crucial factors in successfully crystallising an artificial gemstone is obtaining highly pure starting material, with at least 99.9995% purity. In the case of manufacturing rubies or sapphires, this material is alumina

•VERNEUIL FUSION FLAME METHOD



- O_2 + powdered precursor(s)
- $O_2 + H_2$
- Fusion flame
- Liquid drops of molten precursor(s)
- Growing crystal
- Support for growing crystal

- This starting material is finely powdered, and placed in a container within a Verneuil furnace, with an opening at the bottom through which the powder can escape when the container is vibrated. While the powder is being released, oxygen is supplied into the furnace, and travels with the powder down a narrow tube. This tube is located within a larger tube, into which hydrogen is supplied.

- At the point where the narrow tube opens into the larger one, combustion occurs, with a flame of at least 2000 °C (3,600 °F) at its core. As the powder passes through the flame, it melts into small droplets, which fall onto an earthen support rod placed below. The droplets gradually form a sinter cone on the rode, the tip of which is close enough to the core to remain liquid. It is at that tip that the seed crystal eventually forms. As more droplets fall onto the tip, a single crystal, called a *boule*, starts to form, and the support is slowly moved downward, allowing the base of the boule to crystallise,