Crystal Growth

AN OVERVIEW

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- ***Solids – The materials which has their own volume , Which can not be easily deformed.***
- ***Types of solids:*** ***Crystalline***
  Polycrystalline
  Amorphous
- ***Crystalline : Atoms are arranged in regular & Periodic manner in 3-D with no disruption.***
- ***Polycrystalline: Periodicity is interrupted at grain boundaries at micro level.***
- ***Amorphous:*** ***No regularity, no periodicity.***
- Non crystal: Internal structure is not based on regular repetition pattern.

Man has always admired Crystals , Mighty be due the fact that he always loves beauty.

The Gems and minerals delivered by our earth were always attracted by Human beings.

Since the birth of mankind the gems are used for ornamental purpose.

Gems were also used to decorate the crowns of kings and emperors.

During 15th century, the man has learned the tactics of cutting, cleaving and polishing of Gems to increase their appearance.
The increased appearance arises from their high refractive index and dispersion phenomenon.

If we look at history, the crystalline of salt is known even before the 2700 BC.
In our country the crystallization of Sugar from sugarcane were known by 300 BC.

In 9th & 11th centuary the Arbian alchemist has reported the crystalline of Cupric sulphate and few other salts.

- To day the Crystals are the pillar of Modern technology.
- **With out Crystal there would be no electronic industry, no photonic Industry, no fibre optic communication.**
- **The production of high efficiency photocell, detectors and fabrication of bright long time light emitting diodes for saving energy , the Crystal growth techniques should be perfect.**
- **The Integrated microelectronics, optoelectronics devices needs improved growth technology.**
- **The material used in these devices are GaAs, InP, Silicon and oxides having optimized control of defects.**
- **High temperature and high power electronics demand the material like SiC and GaN.**

- ***High Power LASER Crystals And Radiation Resistance Frequency Multiplying Crystal Of Oxide Compound Are Needed For LASER Fusion.***

  Till today, the high Tc superconductors could not have become possible, either the proper crystal growth technique was not properly developed or neglected.

  In modern technology Physicist, Chemists, Electrical engineers, Metallurgists and Crystal growers are require to assist each other at many levels.

  In fact all these disciplines are interdependent and each one provides special assistance to Crystal Grower.

- Crystal Growth is a vital and fundamental part of material Science and Engineering.
- The crystals of suitable size and perfection are required for fundamental data acquisition and for practical devices such as detectors, Ics, and many other applications.
- In fact behind every new solid state device , there stands a Crystal.
- Now a days the ever increasing demand and application of Semiconductor based electronics needs high quality Semiconducting, Ferroelectric, Piezoelectric and Oxide Crystals.
- On an average, the production of most commonly used domestic electronic material, Silicon is $6x10^4$ Metric Ton per Year , Piezoelectric Quartz is $2.5x10^3$ Metric Ton per Year , GaAs: $1x10^3$ Metric Ton per Year and InP: 10 Metric Ton per Year.

- Day by day the state of art of crystal growth is increasing from 1 inch diameter to 12 inch and then 16 -20 inch diameter of Silicon.
- *The demand of large of crystals are due to the increase in profitability in manufacture of crystal and electronic devices.*
- *Earlier we were fabricating* 10^3 *transistor and now it is possible to fabricate* 10^9 *or even more transistors per chip.*
- *The ever increasing demand of single crystals from the electronic industry has made the science and technology of Crystal growth important.*

- *In fact the silicon wafers are the basis of electronic industry. The total market of Silicon is now more than 10,000 Billion US Doller.*

Crystal Growth Techniques

The crystal growth techniques are classified as;

Growth from Melt

Growth from Solution

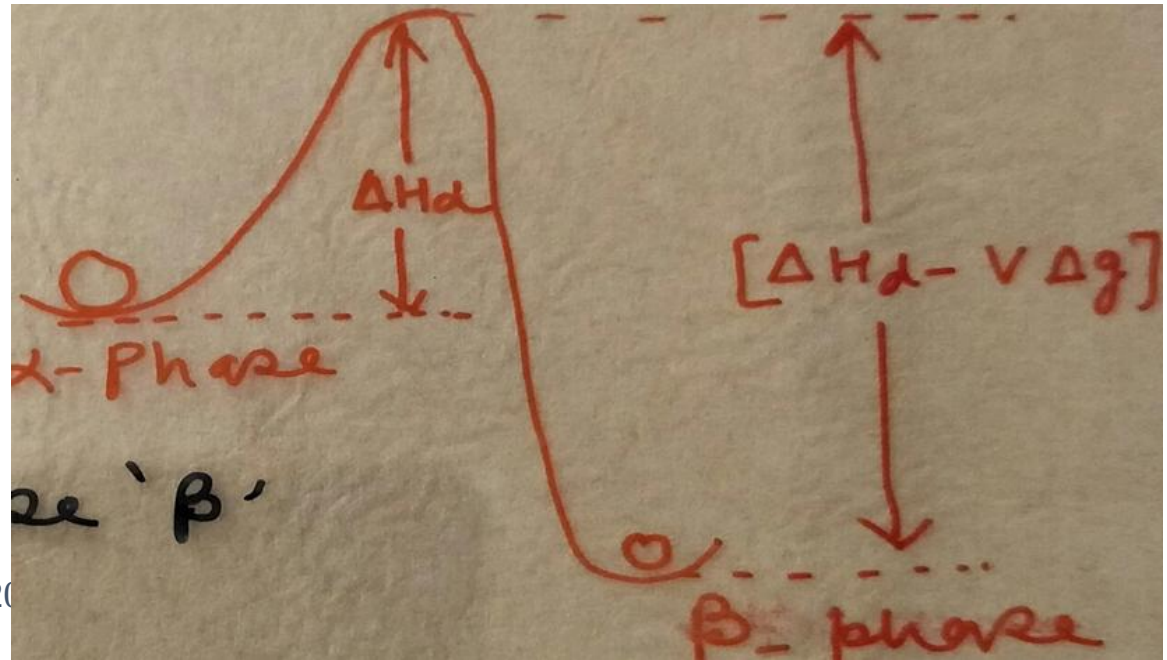
Growth from Vapour

- In fact the good Crystal growth is an ART.
- Because of this the famous book on crystal Growth written by Gilman is

" Art & Science of Growing Crystals"

Growth

- Growth is nothing but the increase in size of the product particle nucleated.
- Consider a transformation “α“ α- β “β”
- The growth process involves an atom leaving “α” and jumping α- β interface to join the product phase “β”
- The activation barrier for “α to β ” is same as the activation energy for diffusion across the interface.



- At equilibrium both α and β have same free energy.

- The frequency of jump from ‘α to β’ and ‘β to α’ are same. The net growth is zero
- At lower temperature the β phase has lower energy, the barrier from β to α jump have higher height. Thus a net flow from α to β takes place. This gives net growth.

- The growth rate U= (dr / dt), “r” is the radius of the particle.

- Crystals are solid substances that may be obtained from Solid, Liquid or Vapours.

Solid Phase

X (solid) Elevated Temperature X (Crystal)

This process is rarely used except for certain metals where strain annealing is effective and where there are change in crystal structure in between room and melting point.

Liquid Phase

A Melt Growth X (solid) Temperature Lowering X (Crystal)

B Flux Growth

X (solid) + Fluxing salt -- Molten State --- X (Crystal)

X (solid) + y (solid) + Fluxing salt -- Molten State --- X (Crystal)

C Hydrothermal Growth

X (solid) + Solvent – High Temp. & Pressure--- X (Crystal)

D Solution Growth

X (solid) + Solvent – Low Temp. & Atm. Pressure --- X (Crystal)

E GEL Growth

X (solid) + Gel medium – Low Temp. & Pressure --- X (Crystal)

A(In solution)+B(in Solution)+Gel medium – Low Temp. & Pressure --- X (Crystal)

F Electro Crystallization

A (in solution) ——————— X (crystal) + Product

Vapour Phase

X (vapour) ——————————— X (crystal)

A (vapour) + B (vapour) ——————— X(Crystal)(with transporting agent)

- This method is used in epitaxial growth of semiconductors.
- The gas phase may be pure or it may contain deliberately added gases to act as transporting agent.

- ***Melt growth techniques are ;***

Crystal Pulling --- Kyropolous and Czochralski

Zone Refining -------Bridgemann and Stober

The factors to be considered in melt growth are;

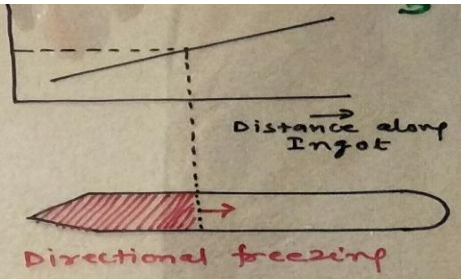
Furnace design, Crucible dimension,
Types of heating, Pull rates, rotation rates, and
Growth direction

Besides these following parameters are also given due consideration;

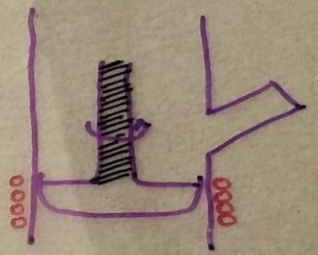
Volatility and Dissociability,
Chemical reactivity and
Melting point

- **Solid phase growth ,**
  some grains grow larger at the expanse of other and the interface is concave w.r.t. the growing grain.
- **In melt growth,**
  the interface takes the shape of isotherm inside the crucible containing the melt.
- **Melt growth is used to grow crystals of those materials which can be melted and than crystallized.**
- **Any crystal growth method should fulfill two requirements:**
  Controlled chemical composition and high degree of physical perfection

The composition of the liquid at the freezing interface moves in the direction of ~~solid~~ shown by arrow at 'C'
Composition of solid is given by arrow at 'D'
Thus the Resulting ingot will be graded in composition.



Normal freezing does not give a single crystal ingot unless a seed crystal is introduced to the melt ⟶ Kyropolous method.



Diameter ; Controlled by heater Power input

Necking ; Used to have single crystal from Polycrystelline seed. which help in reducing the density of dislocation in grown ingot.

Vapour growth Processes

- Sublimation ; solid is passed down the temp. gradient and crystal grows from the vapour phase at the cold end of the tube.
- Vapour transport ; In which the solid material is passed down the tube by a carrier gas
- Gas phase reaction ; In which the crystal grow as a product precipitated from the vapour phase as a result of a chemical reaction between vapour species.

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