

ZONE REFINING

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OUTLINES

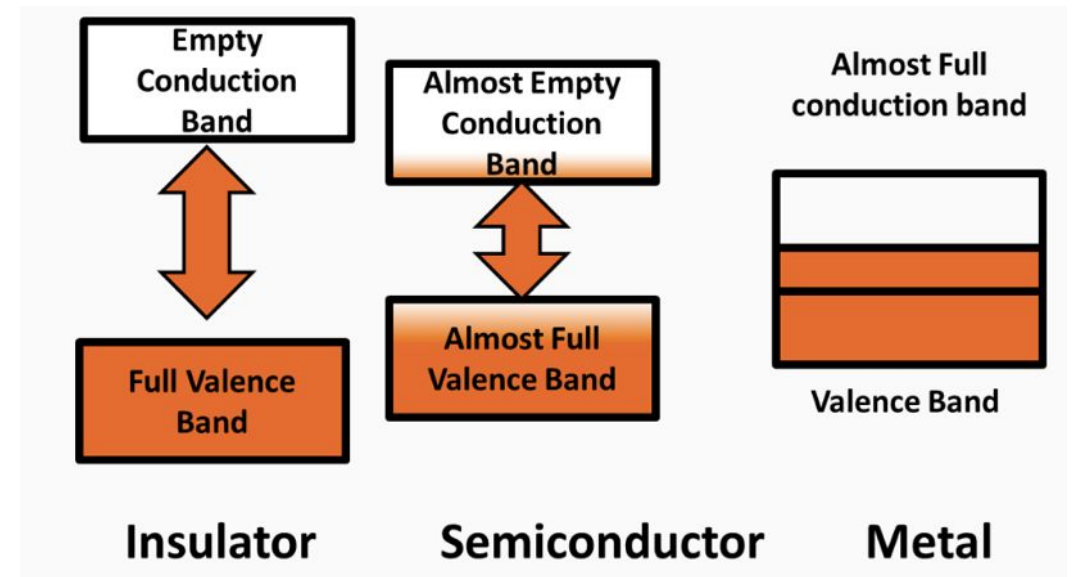
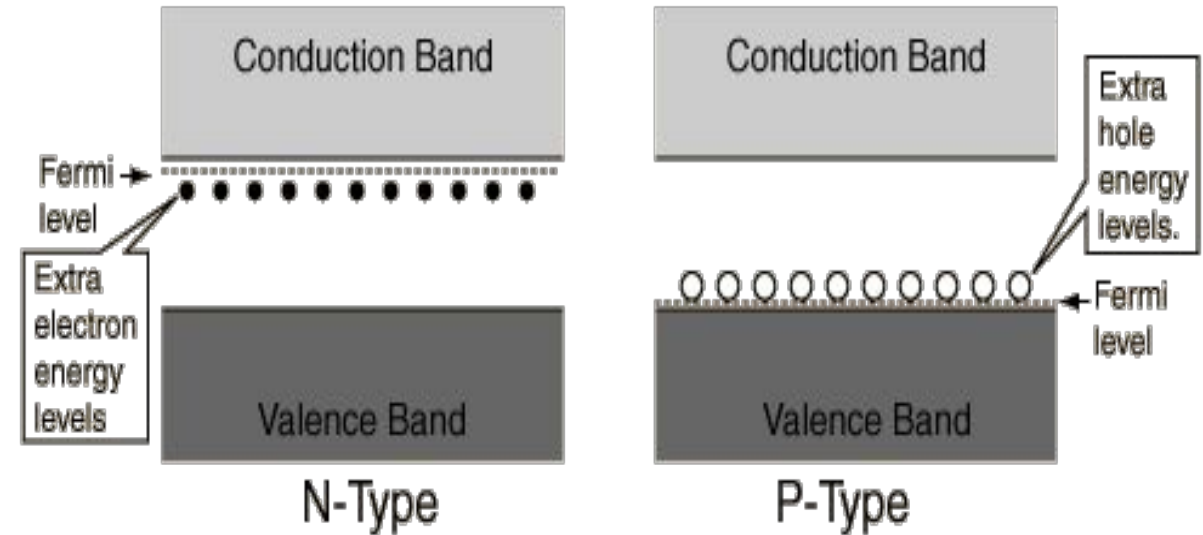
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SEMICONDUCTORS

Semiconductors are materials whose electrical conductivity lie between Conductors and Insulators.

Ex : Silicon and Germanium

- Semiconductors (Si and Ge) have 4 electrons in their outer shell:
2 in the S subshell
2 in the P subshell

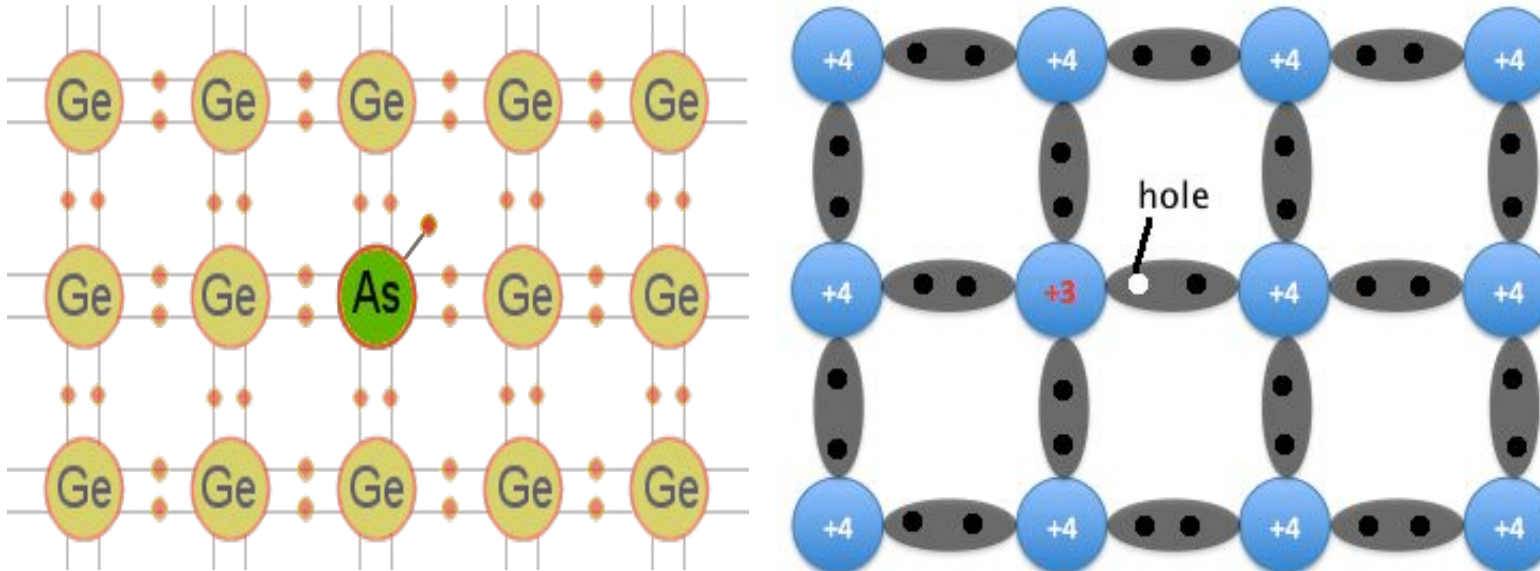


Extrinsic semiconductors

- ❑ The addition of doping elements significantly increases the conductivity of a semiconductor. In fact impurity is accidentally present in semiconductors (even in low concentrations like 1 atom in 10^{12} atoms)

❖ Semiconductors are classified into P-type and N-type

- ❑ P-type: holes are majority carriers i.e. they are positively charged materials
- ❑ N-type: electrons are majority charge carriers i.e. they are negatively charged materials

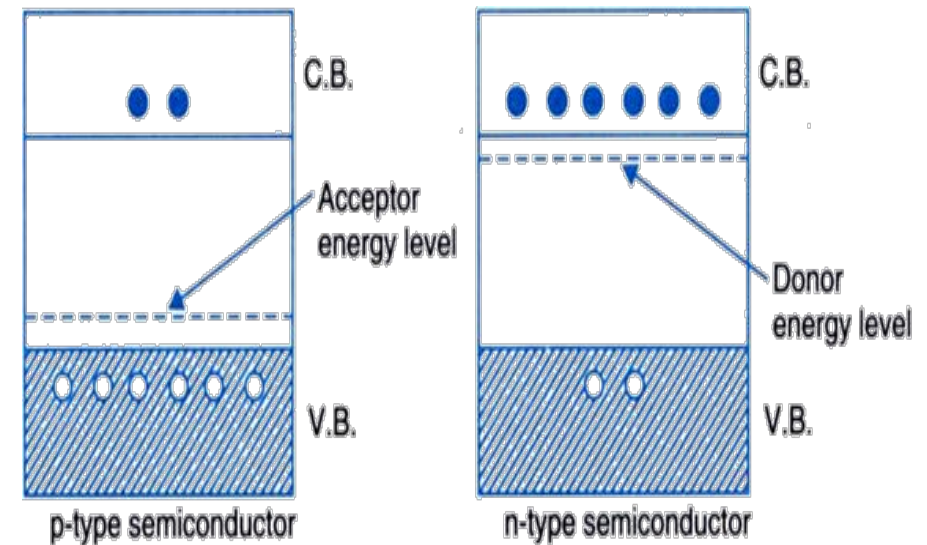
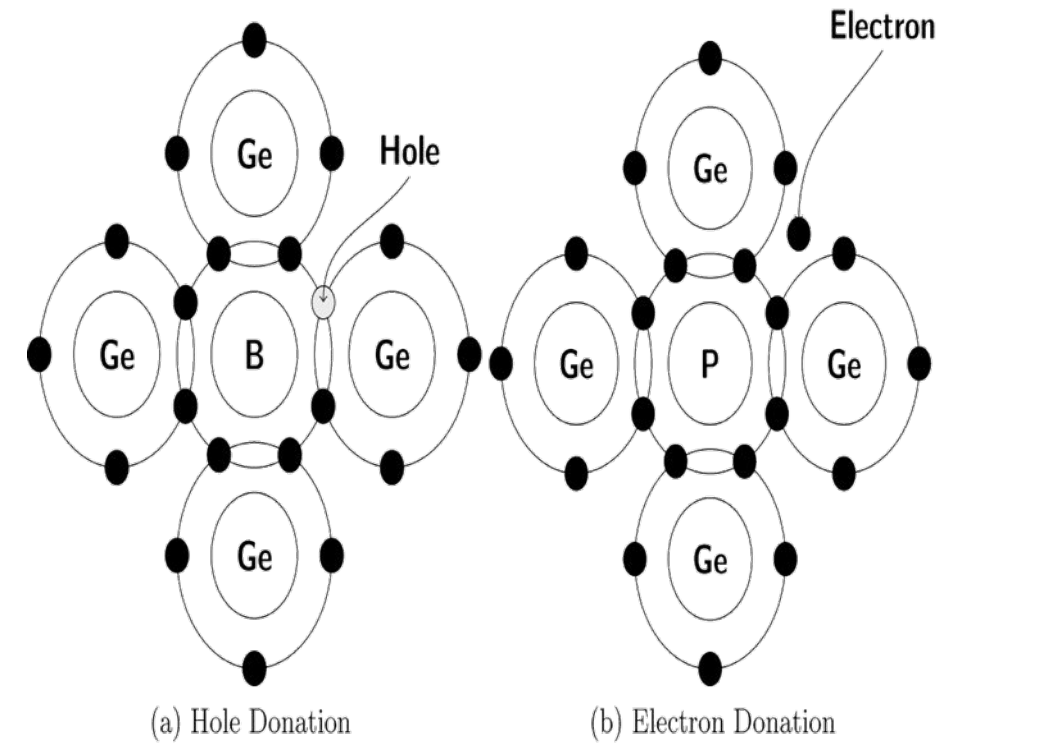


Ionization energies for dopants in Si & Ge (eV)

Type	Element	In Si	In Ge
n-type	P	0.044	0.012
	As	0.049	0.013
	Sb	0.039	0.010
p-type	B	0.045	0.010
	Al	0.057	0.010
	Ga	0.065	0.011
	In	0.16	0.011

Few More Semiconductor's Information

Property	Silicon	Germanium
Structure	Diamond	Diamond
Nearest Neighbor Distance at 300K	0.235 nm	0.245 nm
Density at 300K	2.3290 g.cm ⁻³	5.3234 g.cm ⁻³
Atomic Concentration at 300K	5.00x10 ²² cm ⁻³	4.42x10 ²² cm ⁻³
Linear Expansion Coeff. at 300 K	2.6x10 ⁻⁶ K ⁻¹	5.8x10 ⁻⁶ K ⁻¹
Melting Point	1683 K	1210 K
Electron Hall Mobility at 300 K	1600 cm ² .V ⁻¹ .s ⁻¹ for n = 1.0x10 ¹⁴ cm ⁻³	3900 cm ² .V ⁻¹ .s ⁻¹ for n = 1.0x10 ¹⁵ cm ⁻³
Hole Mobility at 300 K	430 cm ² .V ⁻¹ .s ⁻¹ for n = 1.0x10 ¹⁴ cm ⁻³	1900 cm ² .V ⁻¹ .s ⁻¹ for n = 1.0x10 ¹⁵ cm ⁻³



Fermi Energy Diagram for intrinsic Semiconductor

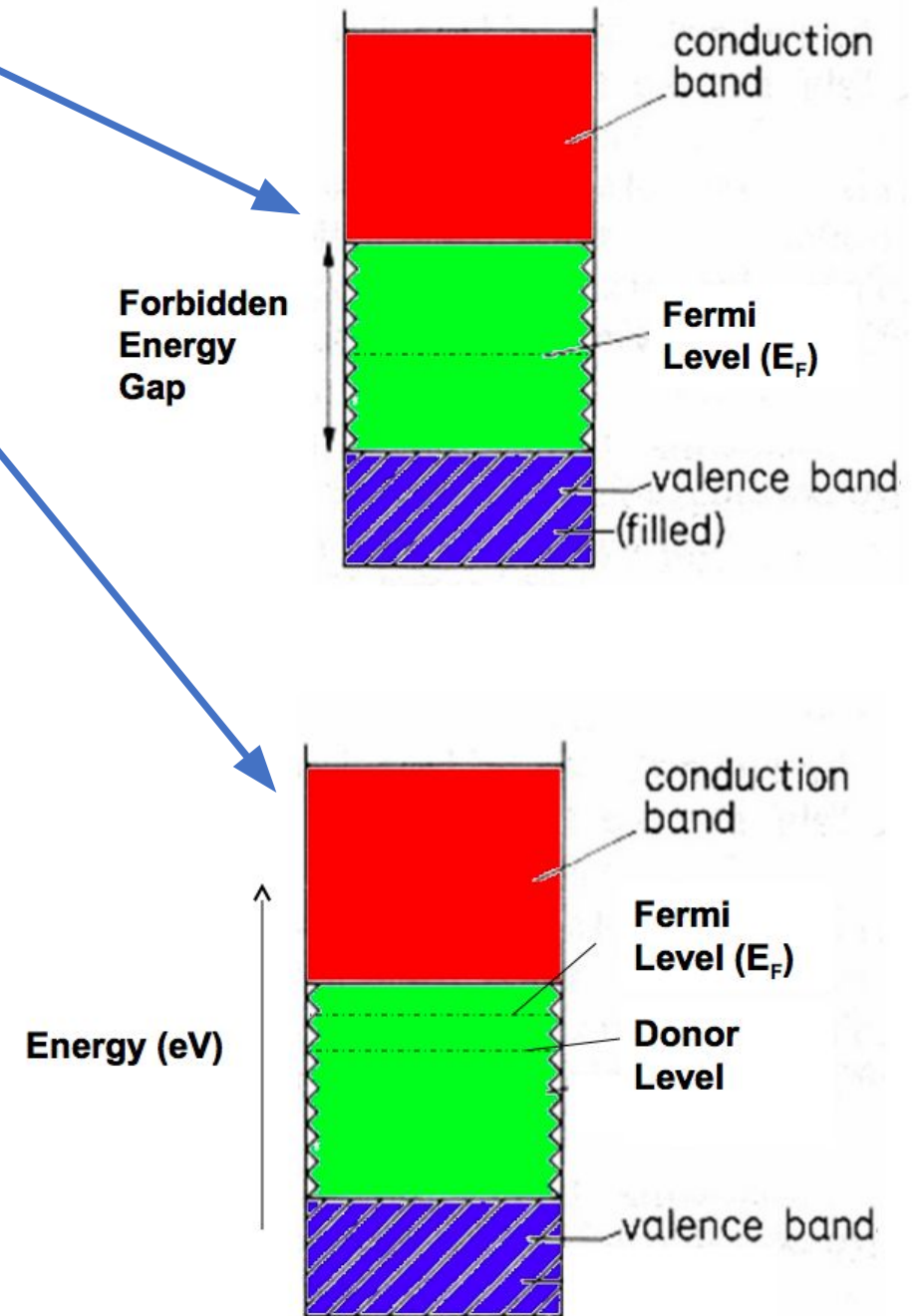
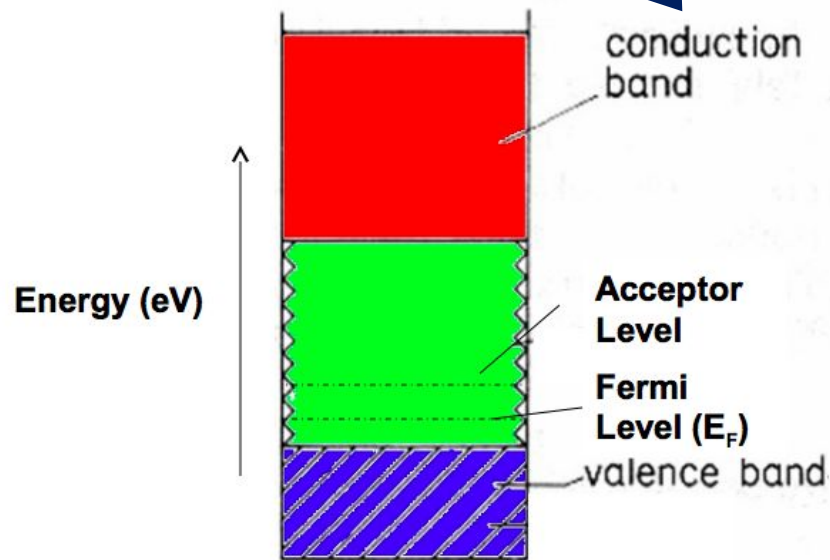
- ❖ The Fermi level (E_F) lies at the center of the forbidden energy gap

Fermi Energy Diagram for N-type Semiconductor

- ❖ The Fermi level (E_F) shifts upwards towards the bottom of the conduction band

Fermi Energy Diagram for P-type Semiconductor

- ❖ The Fermi level (E_F) shifts downwards towards the top of the valence band

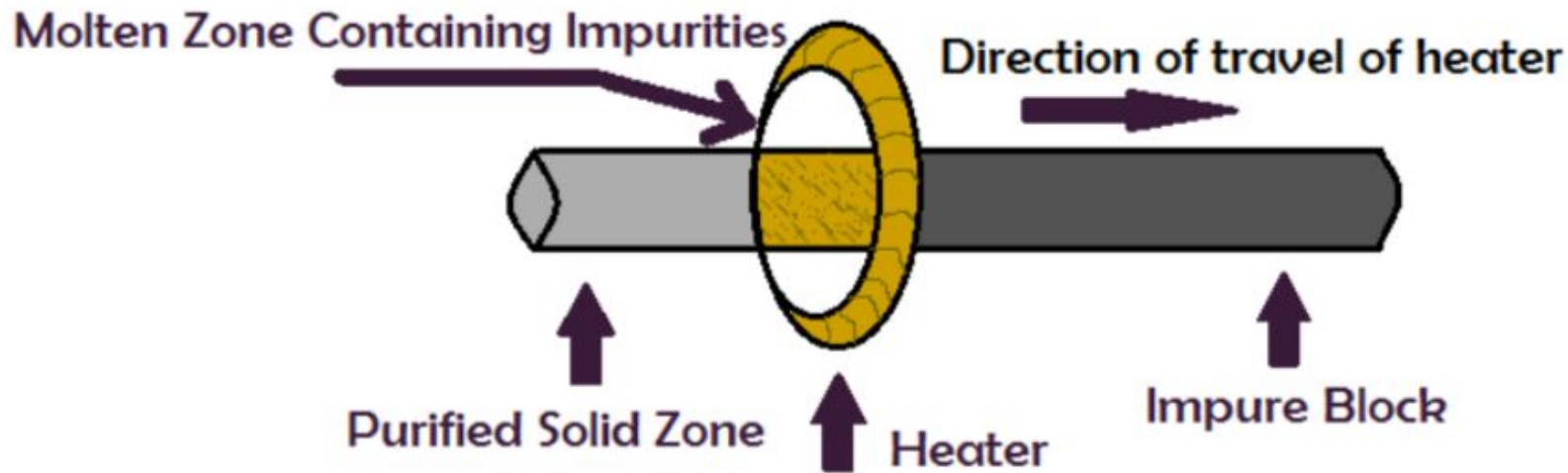


BRIEF HISTORY ON ZONE REFINING

- ❑ zone refining technique was developed at Bell Telephone Laboratories in the year 1950 proposed by Pfann
- ❑ Electromagnetic Stirring in ZR (Stirring molten Zone to disperse the impurity-rich layer at the solid –liquid surface) 1958, Braun,I
- ❑ Separation of Cs and Sr from LiCl-KCl eutectic salt via a zone –refining process for pyro processing waste salt minimization
- ❑ Laser Vacuum Furnace for Zone Refining: (with high-power CO₂ Laser beam to generate precise melt zone 1986, Griner,D.B
- ❑ Purification of Germanium Crystals by Zone Refining: (2016, University of South Dakota)

DEFINITION

Zone refining is a technique to purify materials, mainly semiconductors by melting a short region (*i.e.*, zone) and causing this liquid zone to move slowly through a relatively long rod of the solid.



ZONE LEVELING

- ❖ Effective method for distributing desired impurities uniformly throughout a charge.

Objectives

- (1) Greatest possible uniformity of donor and/or acceptor impurity distribution in the crystal
- (2) Ge crystal lattice with a minimum of imperfections of all kinds.

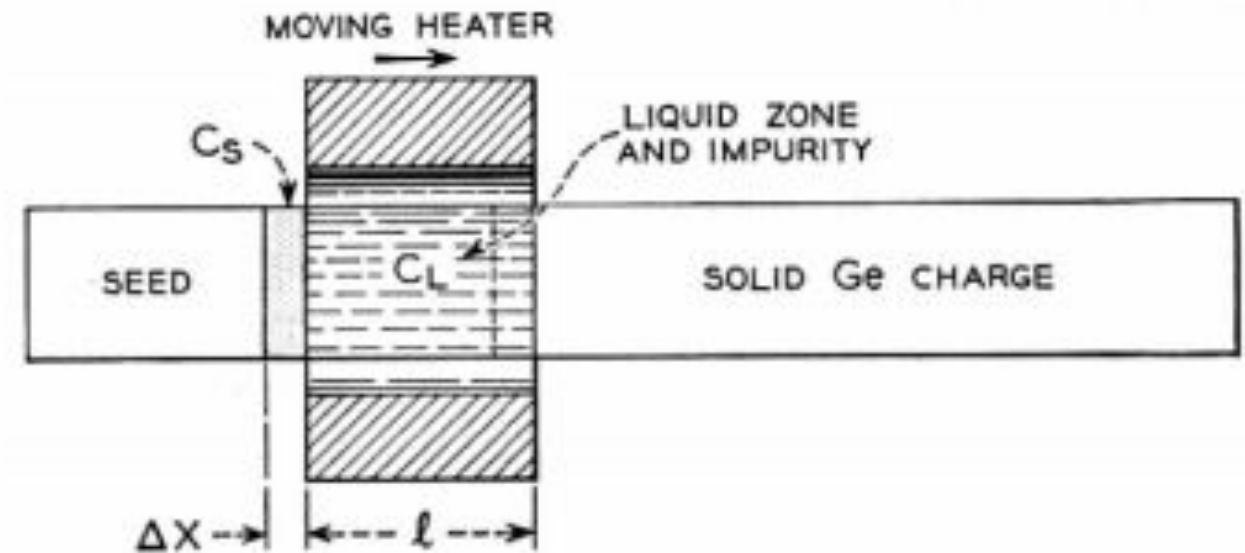


Fig: Schematic of zone leveling operation.

C_L = Concentration of solute in liquid zone
 Δx = Distance moved by liquid zone at right end = Distance moved by frozen germanium at left end
 C_S = Concentration of solute in the frozen zone

$$\text{Distribution Coefficient}(k) = \frac{C_S}{C_L}$$

When $k < 1$, the freezing interface may be regarded as a filter permitting only a fraction k of the solute concentration in the liquid to pass into the growing solid and rejecting the rest to remain in the liquid.

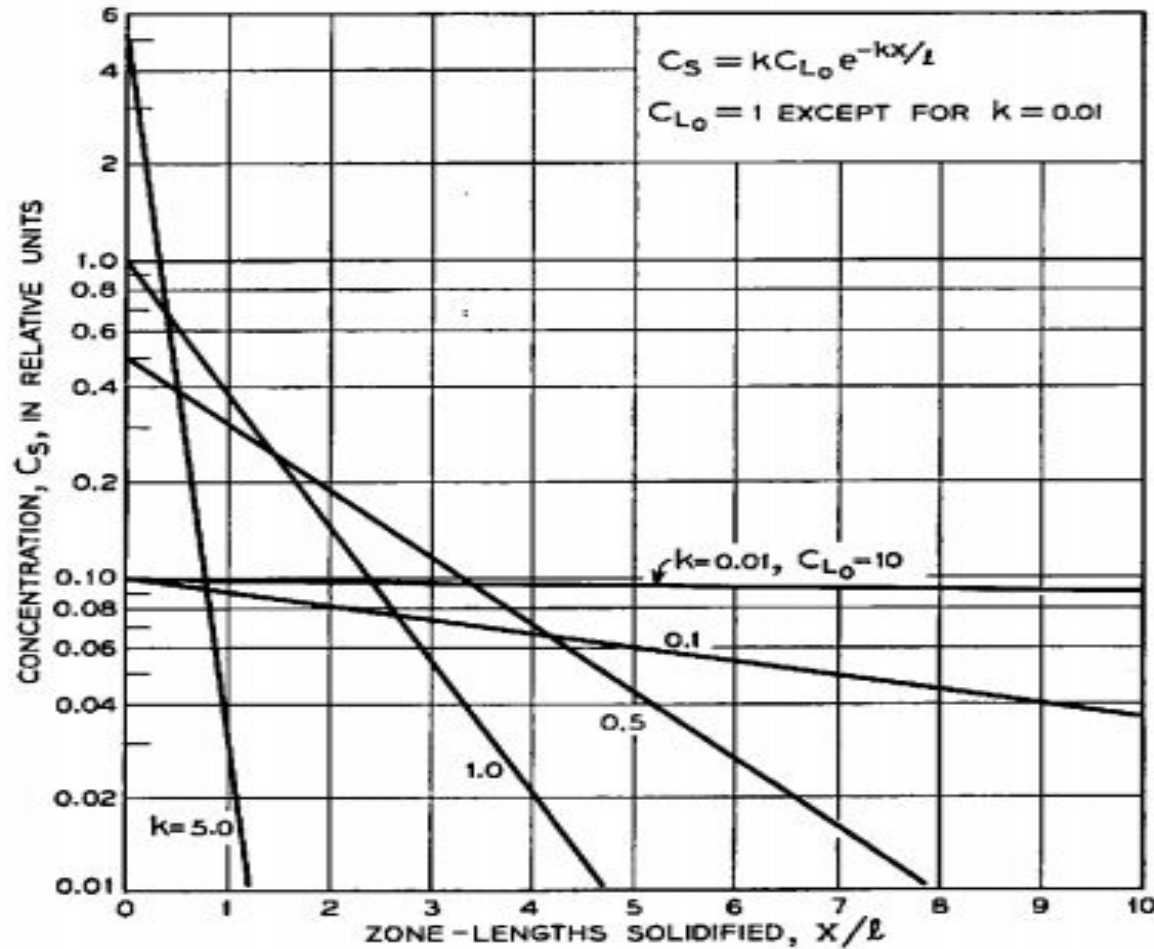
$$C_S = KC_{L_0} e^{-Kx/L}$$

- C_{L_0} is the initial concentration of impurities in the liquid, L is the zone length, and x is the distance moved by the solidifying interface.

Assumption:

- ✓ The liquid volume is constant
- ✓ k is constant.
- ✓ concentration in the liquid is uniform.
- ✓ Diffusion in the solid is negligible.
- when k is small the decay of C_S is slow (i.e., the depletion of C_L is more)

- ❖ It is expected the solute distribution throughout a zone leveled crystal is uniform, in which k is small.



For antimony, $k = 0.003$ as donor, and for indium, $k = 0.001$ as acceptor)

Fig: Solute concentration curves predicted for zone leveling with a starting charge of solute into pure solvent.

REQUIREMENTS ON GERMANIUM FOR SEMICONDUCTOR USES

- At room temperature donors give rise to conduction electrons and the acceptors to conduction holes which are free to move within the germanium crystal.
- If both donors and acceptors are present in the same crystal, the resulting electrons and holes recombine, Net conductivity is contributed by $|N_D - N_A|$
- The conductivity is to be increased by one or two orders of magnitude above the 27°C intrinsic value.

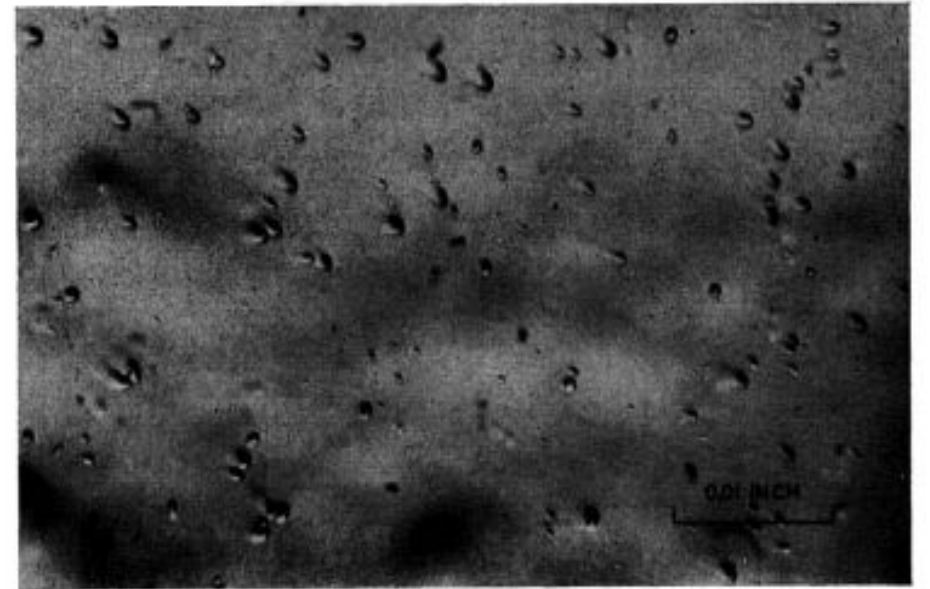


Fig: Microphotograph of Typical Etch Pits on (111) Plane.

Essential to free from lineage, twin, and grain boundaries:

- ◆ **Composition** - Donor-acceptor balance $|N_D - N_A|$ must be accurately controlled: For uniform resistivity
- ◆ **Macro Perfection** - The crystal shall contain no grain boundaries, lineage, or twinning.
- ◆ **Micro Perfection** - The etch pit density must be lower than a certain empirically determined maximum.
- ◆ **Lifetime of Minority Carriers** - Must usually be above a certain minimum

COMPOSITION UNIFORMITY AND CONTROL

- (a) Longitudinal Composition Uniformity
- (b) Cross-Sectional Composition Uniformity

Longitudinal Composition Uniformity

- The primary cause of variations in the longitudinal resistivity is fluctuation of the volume of the liquid zone. For small k , the concentration of solute in the liquid zone, C_L , varies inversely with the zone's volume. If C_L is to be constant, the volume must be constant.

zone volume is directly affected by many variables:

- ✓ temperature fluctuation and drift
- ✓ fluctuation in growth rate
- ✓ variation in the cross-section of the unmelted charge
- ✓ variation in the inert gas flow
- ✓ cracks in the unmelted charge

Resolution:

- ❑ Controlled servo system thermocouple: Sensitivity is $\pm 0.2^{\circ}\text{C}$ at 940°C , With a liquid zone about 4 cm long and a temperature gradient of about 10°C per centimeter at the solidification interface, longitudinal resistivity variations no greater than $\pm 0.3\%$
- To stabilize the temperature gradient fluctuation. It is suggested about $130^{\circ}\text{C}/\text{cm}$ at the melting end of the liquid zone.

Cross-Sectional Composition Uniformity

- Controlling the cross-sectional uniformity is difficult when C_L throughout the liquid is non-uniform.
 - True C_L must always rise locally near the solidifying interface due to the solute diffusion which is necessary when $k < 1$.
- Resolution:**
- by slowing the growth rate
 - by stirring the liquid zone.
- If the maximum is to be no greater than 10 % above the mean, a maximum growth rate of 2×10^{-7} mils per second or 7×10^{-7} inches/hour would be required.
 - Slower the growth rate, smaller will be the diffusion gradient and the higher will be the expected cross-sectional uniformity

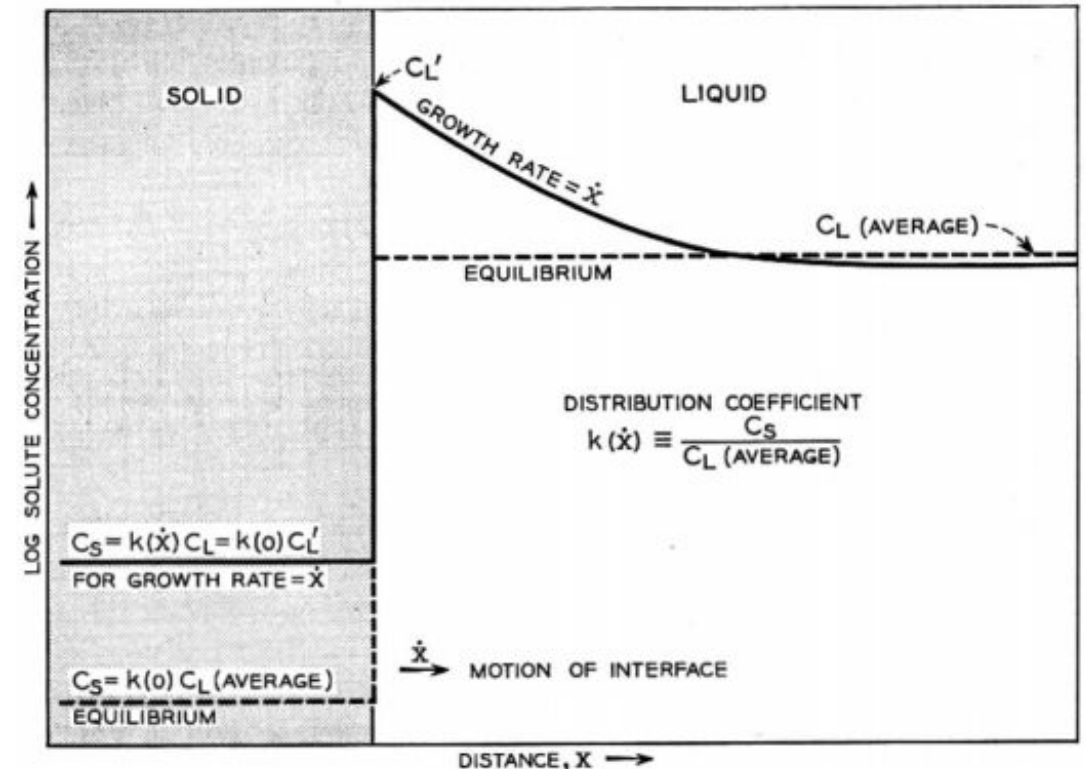


Fig: Solute concentration in solid and liquid at equilibrium and at finite growth rates.

Cont..

- ❑ If the liquid were static (without any currents), it should be possible to obtain a uniform, controlled solute concentration in the solid.

Effective distribution coefficient $K(\dot{x})$ for the given growth rate, \dot{x}

$$K(\dot{x}) = \frac{C_S}{C_L(ave)}$$

- ❑ Presence of convection currents tend to stir the liquid zone and fluctuates in C_S . For this alternative, RF induction heating is used by allowing the RF field to couple directly with the liquid zone. These stirring currents tend to minimize the rise of C_L at the solidification interface and to improve the uniformity of C_L

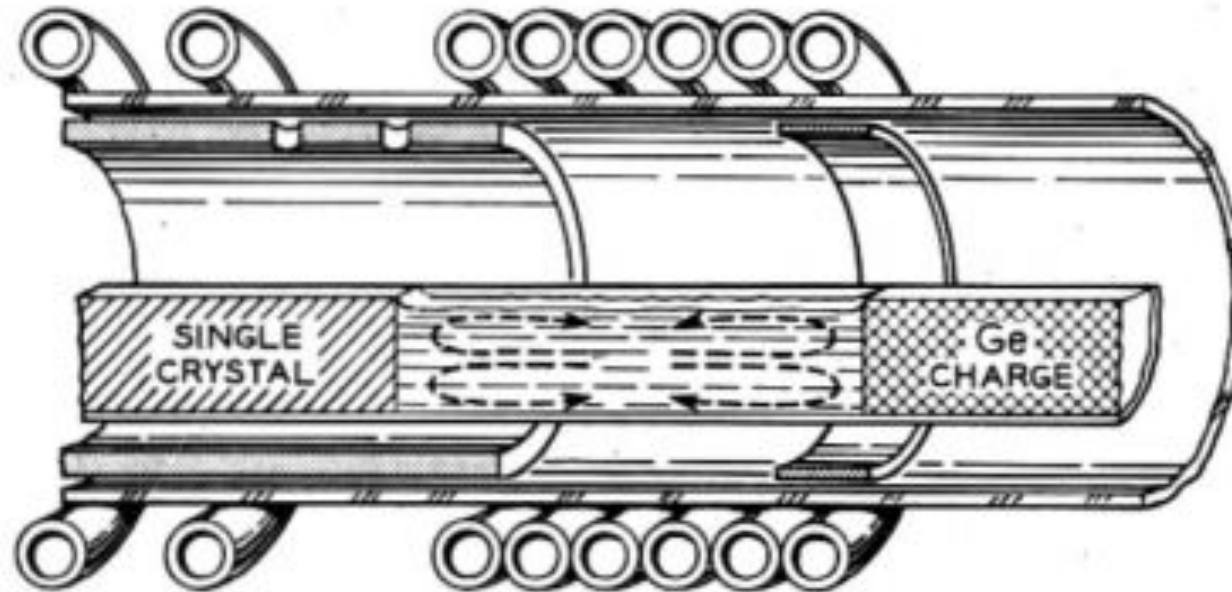


Fig: Stirring currents in liquid induced by RF induction heater.

CRYSTAL LATTICE PERFECTION

- ❖ A lineage boundary (low angle grain boundary) is a set of regularly spaced dislocations, regarded as a surface of p-type material. The dislocation line is believed to have about 4×10^6 per centimeter..

Essential for the growth of a single crystal of high perfection:

- ✓ No stable nuclei form.
- ✓ Temperature of the liquid zone be above its freezing point everywhere except at the interface,
- ✓ Liquid must also be free of foreign bodies that can act as nuclei.
- ✓ Temperature fluctuations are to be avoided.

- Rise in C_L near the solidifying interface, the freezing point is more depressed in this region than that in the bulk of the liquid zone.

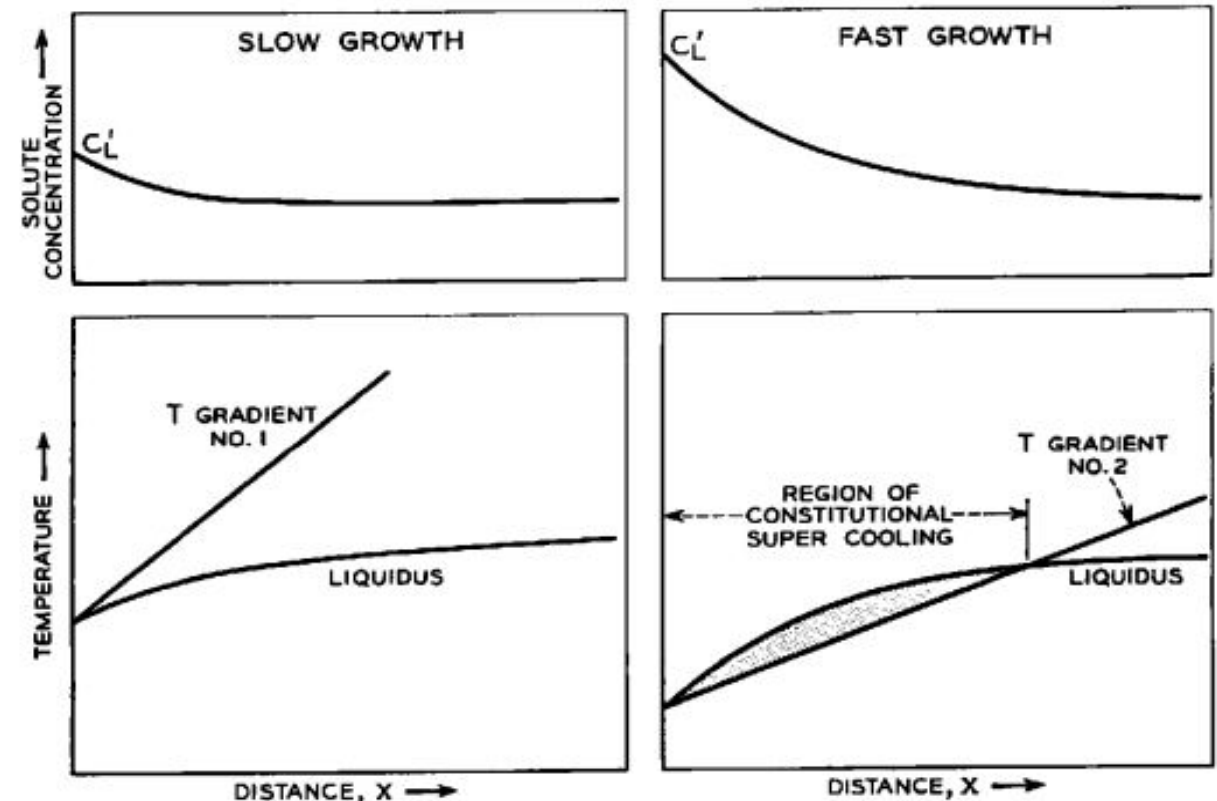


Fig: Solute concentration and temperature curves in liquid, near freezing interface

- ❑ If the temperature gradient is reduced, a region of constitutional supercooling will exist in front of the solidifying interface where nuclei can form and grow.

$\frac{d\theta}{dx} \rightarrow \text{Increase: Decreases(slow) the growth rate}$

$\frac{d\theta}{dx} \rightarrow \text{decrease: Increases(fast) the growth rate}$

- ❖ A foreign body may also initiate polycrystalline growth. A natural site is the wall of the boat
“D. Dorsi” suggested a smoked quartz boat to resolve.

scattered dislocations can be minimized in a single crystal germanium lattice by:

- Selecting the most nearly perfect seeds available
- Slow the growth rates
- Minimizing stresses in the crystal.

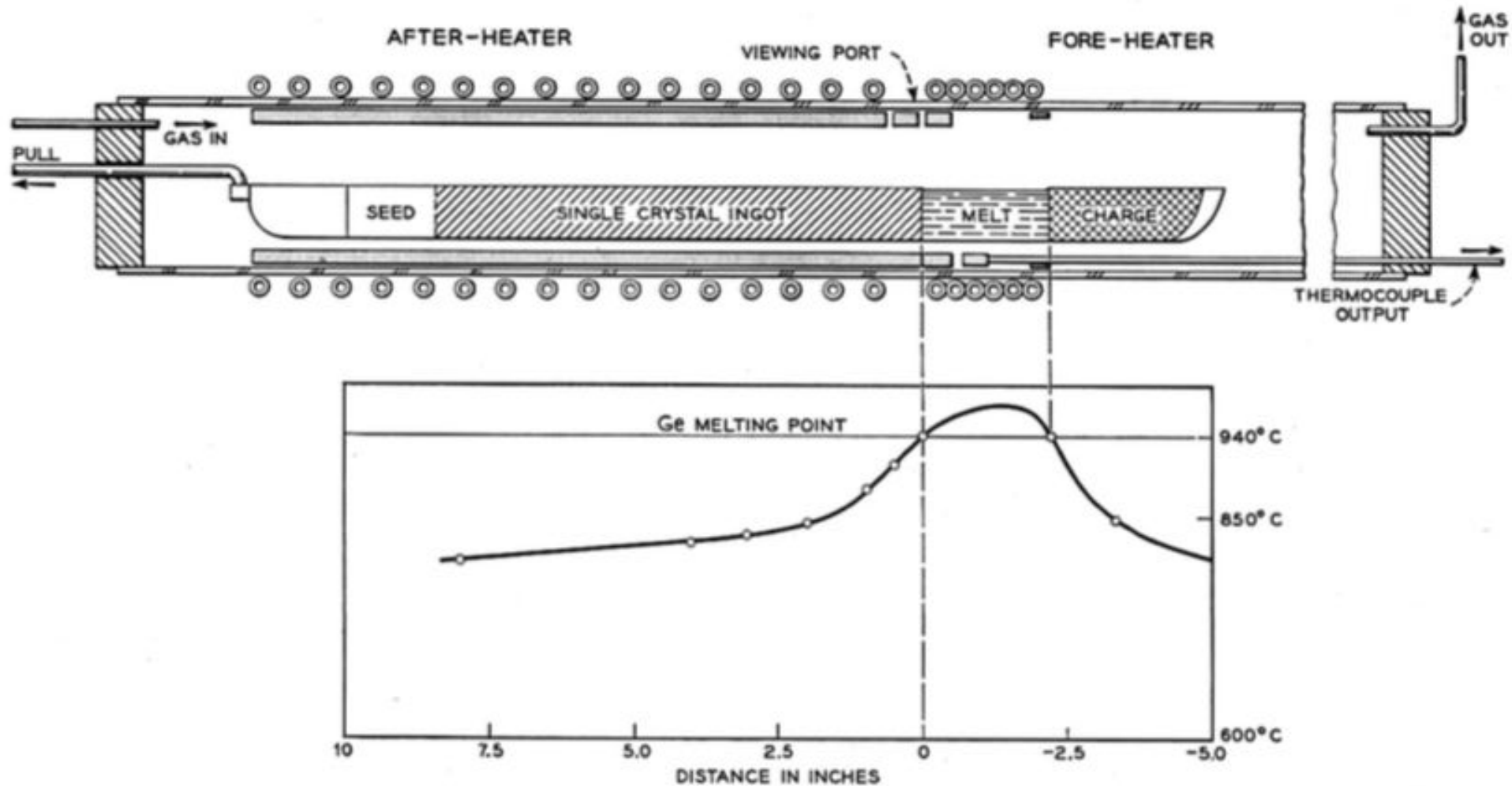


Fig: Axial temperature curve for the germanium zone leveler with after heater

CONT..

- ❑ Heat must enter the crystal by conduction through its hottest surface
- ❑ It must leave through all the other surfaces by radiation and conduction
- ❑ Heat loss does have radial component as well as a longitudinal component to the temperature gradient.
- ❑ The cooler" surface contracts resulting in peripheral tension and internal compression
- ❑ After-heater reduces the heat loss by radiation and radial conduction from the crystal maintaining the entire crystal at a temperature only slightly below its melting point throughout its growth.
- ❑ Temperature gradient at the interface of the leveler is about 10°C per centimeter and the maximum gradient is 30°C per cm

A ZONE LEVELING APPARATUS AND TECHNIQUE FOR GERMANIUM

- Raw materials commercially available are 99.999% pure germanium ingots
- had a resistivity of 50 Ωcm at room temperature
- Electrically active impurity concentration of $10^{13-14}/\text{cm}^3$ at 77 K.
- Raw materials were etched with 1HF:3HNO₃ mixture solution to remove any contamination on the surface
- Rinsed with deionized water 2–3 times, and dried by nitrogen gas

To hold raw Ge high purity graphite boats and ultra-pure synthetic quartz boats are used:

- The quartz tubes were first rinsed with hydrogen peroxide, then rinsed by deionized water 2–3 times and finally dried with nitrogen gas.
- Before the materials were loaded, the graphite boats was cleaned using polyester clothes, and the quartz boats were first etched with 1HF:3HNO₃ mixture solution, then rinsed using deionized water and dried with nitrogen gas
- Coated the inside surface of the quartz boats with carbon using high purity ethylene gas

ZONE REFINED INGOT



Fig: Slices from the zone-refined ingot (last week)



Fig: Slices from the zone-refined ingot

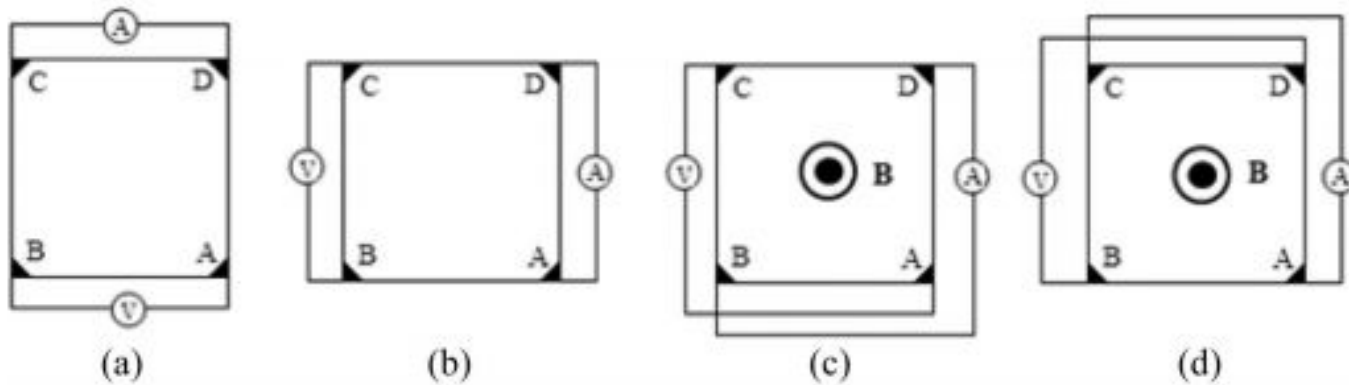
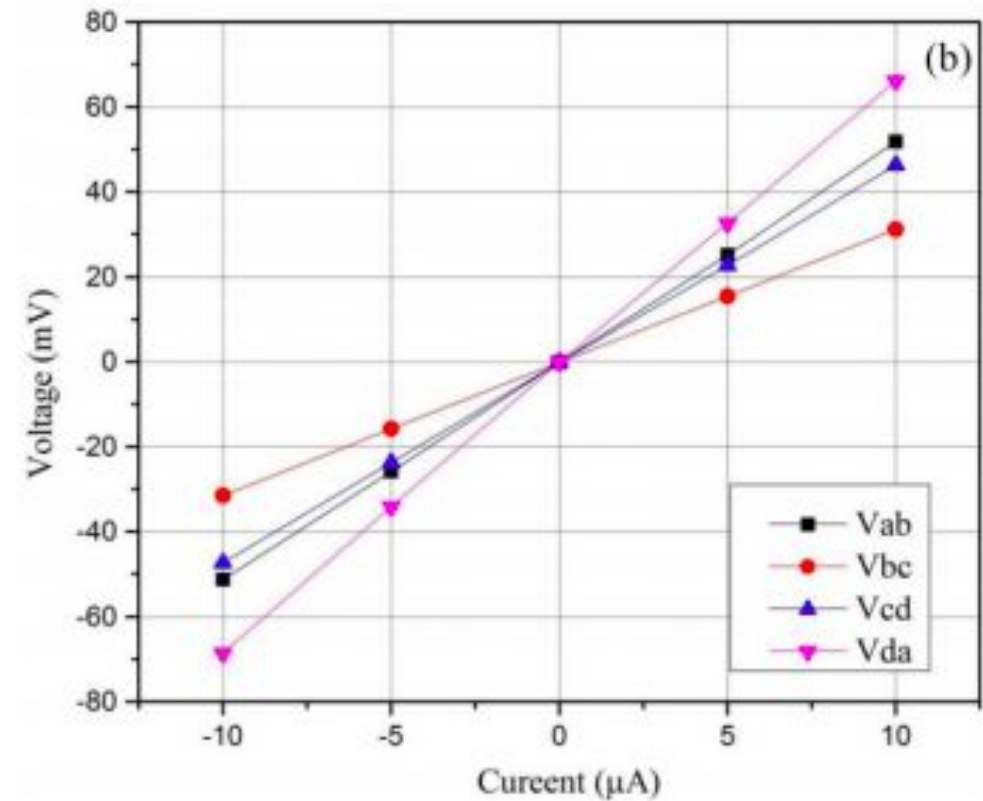


Fig: van de Pauw configuration used to determine resistivity and Hall voltage

- ❑ The van der Pauw Hall measurement was conducted using a Hall measurement system with a 0.55 T permanent magnet, at 77 K
- ❑ In order to identify the type of impurities in the crystals, Photo-thermal Ionization Spectroscopy (PTIS) is applied.
- ❑ The van der Pauw Hall measurement can determine the electrical properties such as: impurity level, mobility of charge carrier and resistivity, and identify conductivity type of semiconductors.
- ❑ Before starting the van der Pauw Hall measurement, we must first measure I-V curve to prove that the electrical contacts are ohmic characteristic



Ref: G Yang et al 2015 J. Phys.: Conf. Ser. 606 012014

Fig: I-V curves for the samples from the zone-refined ingot

Effective segregation coefficient: $K_{eff} = \frac{K}{K + (1-K) \exp(-\frac{V\delta}{D})}$

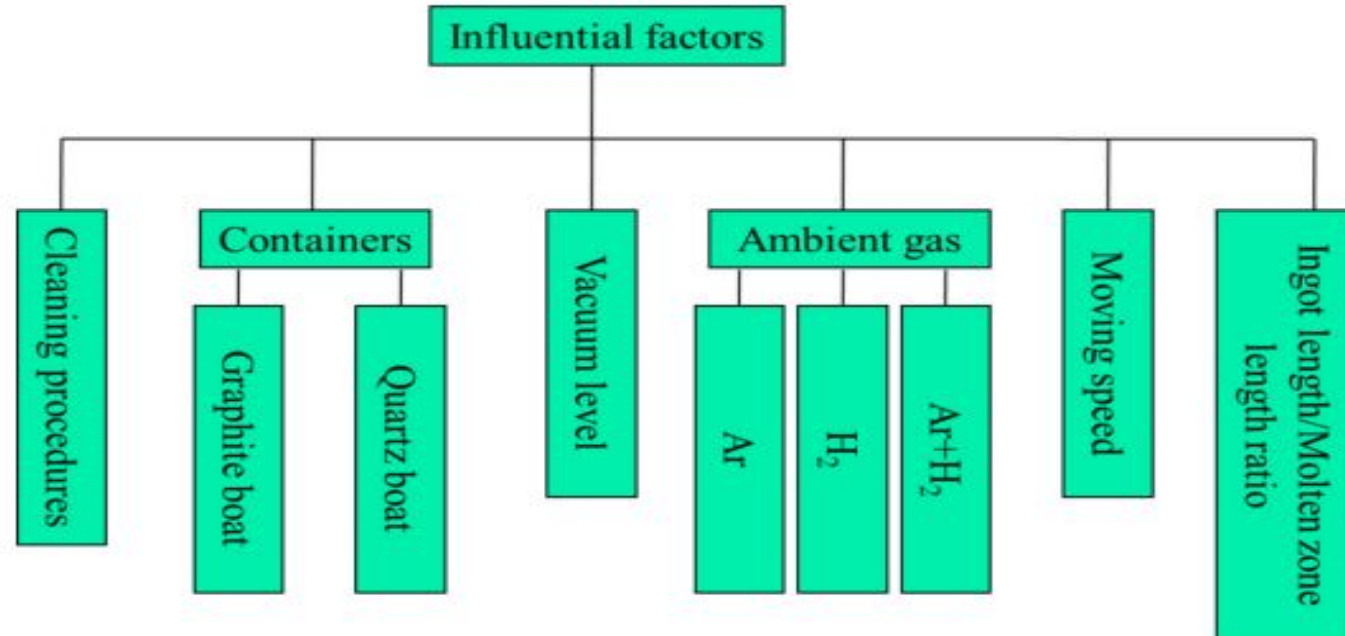
- Boron has a segregation coefficient of approximately 7, indicating that boron aggregates at foremost part of the zone-refined ingot
- Al has a segregation coefficient of approximately 1, when its concentration is around $10^{11}/\text{cm}^3$
- High vacuum levels in the chamber. In our experiments, the vacuum level is typically at 10^{-5} torr

D: impurity diffusion coefficient in the melt

δ : thickness of the diffusion boundary layer

V : zone travel speed.

➤ In order to get high purification, K_{eff} approach K, lower zone travel speed is required



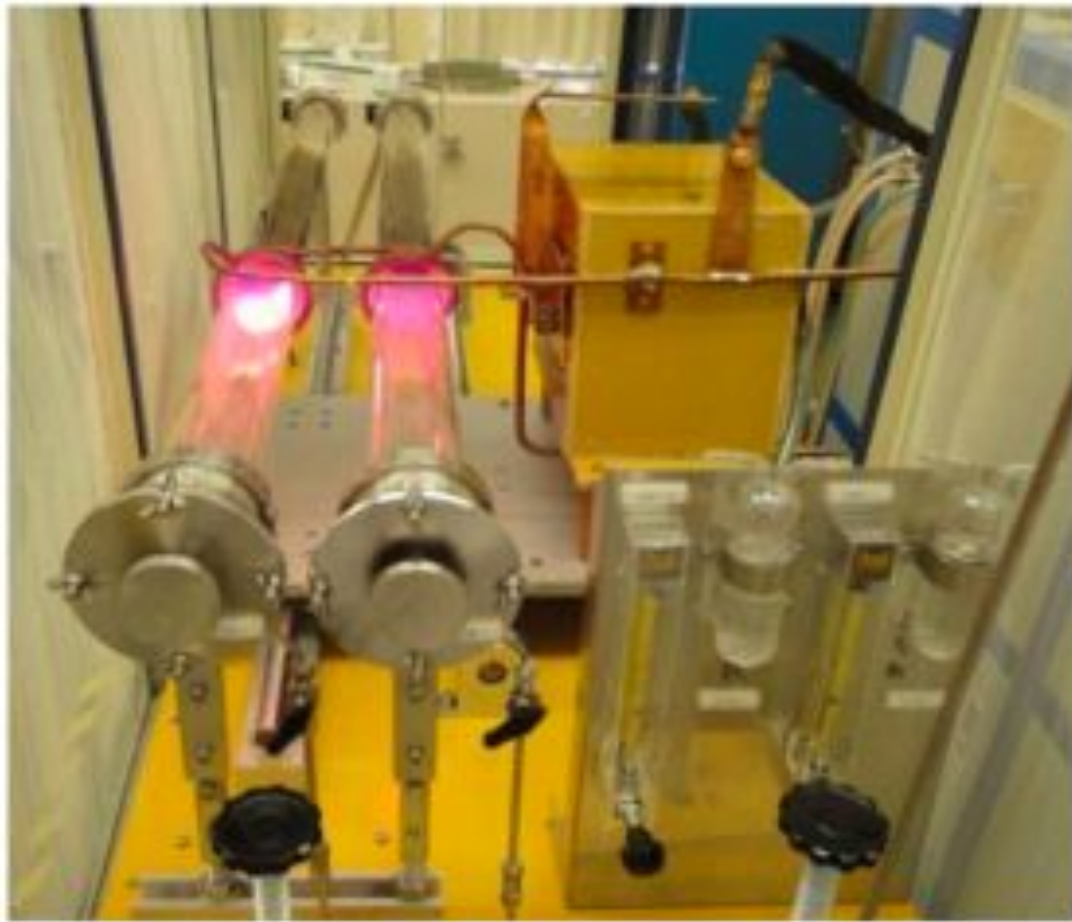
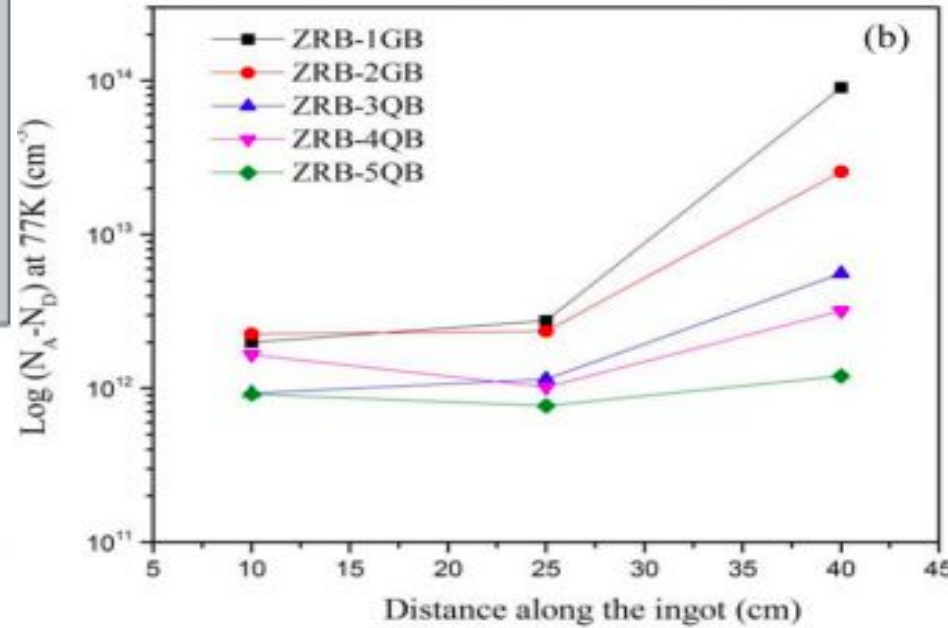
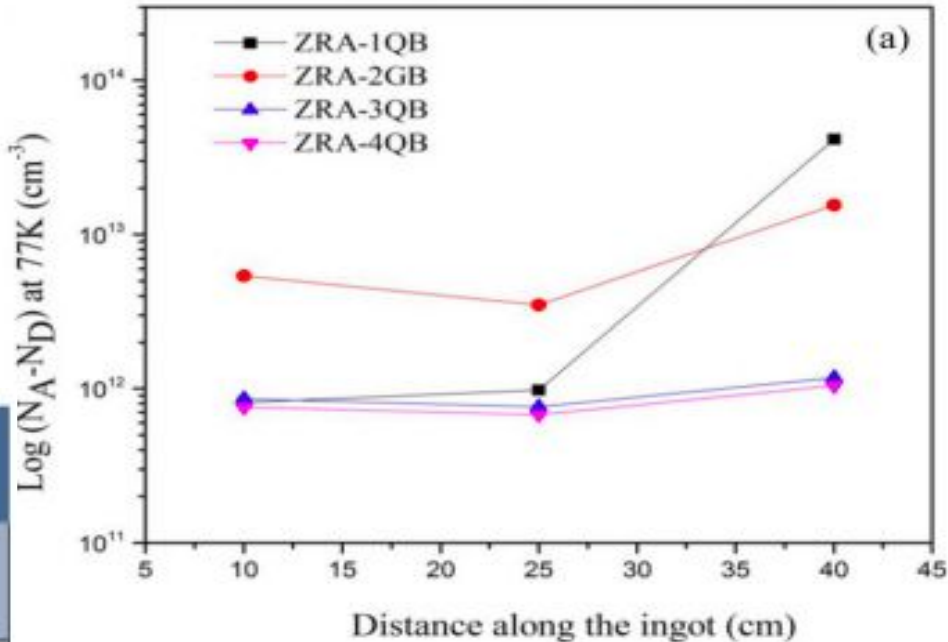


Fig: zone-refiner A (ZRA) and zone-refiner B (ZRB). They have the capacity of 4 Kg and 16 Kg, respectively. Each tube has single induction coil for heating. The heating power supply is high frequency (200kHz) induction heating source

Positive carrier concentrations → P-type germanium crystals

Table 1 Three main impurities in HP germanium crystals

	Source	Segregation coefficient (K)	Distribution	How to remove	Possible compounds
Boron (B)	Raw materials, Graphite boat, Carbon-coated quartz boat	>1	Initial part of the refined ingots	Zone refining in silane-produced carbon-coated Quartz remove B impurity down to $\sim 10^{10}/\text{cm}^3$	Boron Oxide
Phosphor (P)	Raw materials, Graphite boat, Carbon-coated quartz boat	<1	Mainly in the tail part of the refined ingots	Easy to remove by zone-refining	N
Aluminum (Al)	Raw materials	~ 1	Along the entire refined ingots	Zone-refining in graphite boat	Al-o complexes



MAIN USAGE

Ge Detectors:

HPGe crystal can be used to fabricate thick radiation detectors.

REQUIREMENTS:

- Net impurity level of 10^{10} cm^{-3}
- Dislocation density between 10^2 and 10^4 cm^{-2} throughout the entire crystal

Investigation:

- ✓ Dark matter and Neutrinos.
- ✓ Neutrino less double-beta decay event.

CONCLUSION

- ❑ The segregation coefficient equation is not concerned with lattice imperfections in the ingot such as dislocations, lineage, or grain boundaries.
- ❑ 7–8 cm per hour is an ideal zone travel speed, and the best ratio for ingot length to molten zone length was 1/15 to 1/20.
- ❑ The results indicate that ingots zone-refined in quartz boats have a higher purity level than those in graphite boats
- ❑ After zone-refined in graphite boat, the impurity level decreased by a factor of 10 to 100 from the raw materials with impurity level of $10^{13-14}/\text{cm}^3$ to $10^{12}/\text{cm}^3$. The zone-refining in quartz boat further decreased the impurity level to $10^{11}/\text{cm}^3$ by a factor of 10.
- ❑ Results obtained from after heater at the "slow" growth rate of 0.09 mils per second found: Compositional Uniformity Macro Perfection(no cases of polycrystallinity, or twinning except few cases of lineage & rise in Lifetime of Minority Carriers.

THANK YOU