### KARPAGAM ACADEMY OF HIGHER EDUCATION

#### SEMESTER – I

#### 17PHP105A

#### MATERIAL SCIENCE

L T P C 4 - - 4

**Scope:** Study of materials is always important, for any application, including fabrication of satellites. It is important to know the basics of materials and their formation, for a physics student.

**Objectives:** This paper gives a basic picture about the nature and formation of different materials.

#### UNIT - I

**Nature of thin films:** Deposition technology – Distribution of deposits – Resistance heating – Thermal evaporation – Flash evaporation.

Electron beam method – Cathodic sputtering – Glow discharge sputtering – Low pressure sputtering – Reactive sputtering – R. F. sputtering – Chemical and Physics vapor deposition – Chemical deposition.

**Thickness Measurement Methods:** Mass methods – Optical method – Photometric – Ellipsometry – Interferometry – Other methods – Substrate cleaning.

#### UNIT- II

**Electron Diffraction Technique:** Electron diffraction technique – High energy electron diffraction – Low energy electron diffraction – Electron microscopy – Scanning electron microscopy – X-ray photoelectron spectroscopy – Mass spectroscopy – Thermodynamics of nucleation – Nucleation theories – Film growth – Incorporation of defects, impurities etc. in film – Deposition parameters and grain size.

### UNIT – III

**Single Crystals:** Significance of single crystals – Crystal growth techniques – The chemical physics of crystal growth – crystal growth phenomena – Nucleation – Gibbs Thomson equation – for vapor – for solution – Spherical nucleus – Heterogeneous nucleation – Cap shaped nucleus – Disc shaped nucleus – Characterisation techniques – XRD spectra and Analysis.

#### UNIT IV

**Singular and rough faces:** Models on surface roughness – The Kossel, Stranski, Volmer (KSV) theory – The Burton, Cabrera and Frank (BCF) theory – BCF theory of solution growth – Periodic Bond chain theory – the Muller – Krumbhaar Model.

The Bridgman and related techniques – Crystal pulling techniques – Convection in melts – Modeling and simulation of bulk crystal growth considering melt dynamics – Melt growth of oxide crystals for saw, piezo electric and non linear optical applications – Liquid encapsulated and Czochralski technique – Zone melting technique – Skull melting process – Heat exchanger method.

### UNIT V

**Nanotechnology:** An introduction – Nanodevices – Carbon nanotubes – Types of Carbon Nanotubes: Single walled, Multiwalled, Torus – Properties: Hardness – Strength – Electrical – Thermal – Optical – Synthesis – Arc discharge – Laser Ablation.

## **TEXT BOOK:**

- 1. Goswami. A., , 1<sup>st</sup> Edition 2014, Thin film fundamentals, New Age International Pvt Ltd, New Delhi.
- 2. Santhanaragavan. P and P. Ramasamy, 2<sup>nd</sup> Edition 2012, Crystal Growth Processes and Methods, KRU Publications, Kumbakonam.

### **REFERENCES:**

- 1. Meissel. L.T and R. Glang., 2006, Hand book of thin film technology, Tata McGraw Hill, New Delhi.
- 2. Shalini Suri, 1<sup>st</sup> edition 2006, Nano Technology: Basic Science to Emerging Technology, Aph Publishing Corporation.
- 3. Brice. J.C., 1<sup>st</sup> edition, 2003, Crystal growth processes, John Wiley and Sons, New York

### KARAPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE-21

#### **DEPARTMENT OF PHYSICS**

### LECTURE PLAN (2017-2018 ODD SEMESTER)

#### I M.SC PHYSICS (2017-2019 BATCH)

### MATERIAL SCIENCE (17PHP105A)

#### $\boldsymbol{UNIT-I}$

Lecture Duration (Hr)	Topics to be Covered	Support Materials
1 Hr	Deposition Technology, Distribution of deposit	T1(4-5), T1(7- 10)
1 Hr	Resistance Heating	T1(11-12)
1 Hr	Flash Evaporation	T1(18-19)
1 Hr	Electron beam method, Cathodic sputtering	T1(19-20), T1(20-21)
1 Hr	Glow discharge sputtering	T1(22-23)
1 Hr	Low pressure sputtering, Reactive sputtering, RF sputtering	T1(27), T1(27- 28), T1(28-29)
1 Hr	Chemical and physical vapor deposition, chemical deposition	T1(29-30), T1(31-32)
1 Hr	Mass method, optical method	T1(36-38), T1(38-40)
1 Hr	Photometric, Ellipsometry	T1(40-41)
1 Hr	Interferrometry, other methods, substrate cleaning	T1(42-43), T1(45-46)
1 Hr	Revision	
	Total number of Hours planned for Unit - I	11 Hrs

#### **Text Book**

T1 – Goswami. A., Ist Edition, 2014. Thin film Fundamentals, New Age International Publishers Private Limited

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Lecture	Topics to be Covered	Support
Duration		Materials
(Hr)		
1 Hr	Electron diffraction Technique	T1(111-112)
1 Hr	High energy electron diffraction	T1(112-114)
1 Hr	Low energy electron diffraction, Electron microscopy	T1(114-116),
		T1(118-119)
1 Hr	Scanning electron microscopy	T1(128-130)
1 Hr	X-ray photoelectron spectroscopy, Mass spectroscopy	T1(135-136),
		T1(136)
1 Hr	Thermodynamics of nucleation	T1(141-142)
1 Hr	Nucleation theory	T1(145-146)
1 Hr	Film growth, Incorporation of defects	T1(156-157)
1 Hr	Deposition parameters	T1(161-162)
1 Hr	Grain size	T1(162)
1 Hr	Revision	
	Total number of Hours planned for Unit - II	11 Hrs

# UNIT - II

### **Text Book**

T1 – Goswami. A., Ist Edition, 2014. Thin film Fundamentals, New Age International Publishers Private Limited

Lecture Duration	Topics to be Covered	Support Materials
(Hr)		
1 Hr	Significance of single crystals, Crystal growth techniques	T2(4-6), T2(13-
		14)
1 Hr	Chemical physics of crystal growth	T2(15-16)
1 Hr	Crystal growth phenomenon	T2(19)
1 Hr	Nucleation	T2(19-20)
1 Hr	Gibbs Thomson Equation for vapor and solution	T2(22-25)
1 Hr	Spherical nucleus	T2(26-27)
1 Hr	Heterogeneous nucleation	T2(30-31)
1 Hr	Cap shaped nucleus	T2(31-32)
1 Hr	Disc shaped nucleus, characterization technique	T2(33-34)
1 Hr	XRD spectra and analysis	T2(37-38)
1 Hr	Revision	
,	Total number of Hours planned for Unit - III	11 Hrs

# UNIT - III

## **Text Book**

T2 - Santhanaragavan P., and P. Ramasamy, Ist Edition, 2012. Crystal growth processes and methods, KPU publications, Kumbakonam.

Lecture	Topics to be Covered	Support Motorials
(Hr)		Water lais
1 Hr	Models on surface roughness, Kossel, Stranski, Volmer	T2(40-41),
	(KSV) theory	T2(42-46)
1 Hr	Barten, Cabrera and Frank (BCF) theory	T2(49-53)
1 Hr	BCF theory for solution growth, periodic chain bond theory	T2(56-57),
		T2(57-58)
1 Hr	The Muller-Krumbharr model	T2(63-65)
1 Hr	Bridgmann and related techniques, crystal pulling technique,	T2(75-76),
	convection in melts	T2(79-80),
		T2(92-93)
1 Hr	Modeling and simulation of bulk crystal growth considering	T2(103-104)
	melt dynamics	
1 Hr	Melt growth of oxide crystals for saw, piezo electric and	T2(109-110)
	non-linear optical applications	
1 Hr	Liquid encapsulated and Czechralski technique	T2(116-118)
1 Hr	Zone melting technique	T2(123-134)
1 Hr	Skull melting process	T2(129-130)
1 Hr	Heat exchanger method	T2(139-140)
1 Hr	Revision	
,	Total number of Hours planned for Unit - IV	12 Hrs

# $\mathbf{UNIT} - \mathbf{IV}$

### **Text Book**

T2 - Santhanaragavan P., and P. Ramasamy, Ist Edition, 2012. Crystal growth processes and methods, KPU publications, Kumbakonam.

Lecture Duration	Topics to be Covered	Support Materials
(Hr)		
1 Hr	Nanotechnology – an introduction	T1(390)
1 Hr	Nanodevices	T1(391-392)
1 Hr	Carbon nanotubes	T1(394-395)
1 Hr	Types of carbon nanotubes	T1(395-396)
1 Hr	Single walled, multi walled, torus nanotubes	T1(396-398)
1 Hr	Properties	T1(399)
1 Hr	Hardness	T1(400)
1 Hr	Strength	T1(401-403)
1 Hr	Electrical, thermal and optical properties	T1(404-405)
1 Hr	Synthesis – Arc discharge	T1(406)
1 Hr	Laser ablation method	T1(407-408)
1 Hr	Revision	
1 Hr	Old question paper discussion	
1 Hr	Old question paper discussion	
1 Hr	Old question paper discussion	
	Total number of Hours planned for Unit - V	15 Hrs

# $\mathbf{UNIT} - \mathbf{V}$

### **Text Book**

T1 – Goswami. A., Ist Edition, 2014. Thin film Fundamentals, New Age International Publishers Private Limited

**Nature of thin films:** Deposition technology – Distribution of deposits – Resistance heating – Thermal evaporation – Flash evaporation.

Electron beam method – Cathodic sputtering – Glow discharge sputtering – Low pressure sputtering – Reactive sputtering – R. F. sputtering – Chemical and Physics vapor deposition – Chemical deposition.

**Thickness Measurement Methods:** Mass methods – Optical method – Photometric – Ellipsometry – Interferometry – Other methods – Substrate cleaning.

# **Deposition technology**

## **Distribution of deposit**

Evaporate molecules issuing out from heated sources will spread out in all directions but their velocity distributions will depend on the nature of the source which can be broadly classified as (i) point source (ii) surface source (iii) cylindrical source.

(i)If a source can be approximated to a tiny sphere compared to its distance from the receiving substrate, then the emitted vapor stream will have the same velocity distribution in all direction thus resembling the emission from a point source such a type of source is known as the point source.

For (ii), the emission velocity of the vapor stream will be directional and maximum along the source normal direction but it will decrease with increase of the angle of inclination ( $\psi$ ) of the direction with the source normal. The velocity distribution will follow the cosine law and decrease with increase of  $\psi$  such a source is called a directed surface source. If  $\psi$ =0, then a surface source resembles a point source except that it is not spherical in the category (iii), the emission of vapor stream will be from the surface of a cylinder and can be approximately between an idealized point source and a surface source.

There are several types of practical heating sources made from refractory metals such as tungsten, molybdenum, tantalum etc. and their emission characteristics can be approximated to one of the above three categories.

There source may be made from single or multi stranded filaments to various shapes or from straight strips with or without any dimple at the centre or in the form of a boat and sometimes having the shape of a cylinder etc..(Fig. a,b,c,d).



Fig 1. Evaporation source of different types:

a-hair pin type, b- wire helix, c- wire basket, d- dimple foil, e-dimple foil with refractory oxide coating, f- canoe type.

The amount of deposits received by a substrate will depend not only on the nature of the source but also on the inclination of the vapor stream ( $\theta$ ) with the substrate normal direction. Let us now consider the amount of material (dm), that will be emitted through a solid angle d $\omega$  of a source which may be in the form of a point or surface source. If m is the total amount of the material evaporated, then for the case (i), i.e point source

$$dm = \frac{m}{4\pi} d\omega \tag{1}$$

Case (ii) i.e surface source

$$dm = \frac{m}{\pi} \cos\varphi d\omega \tag{2}$$

If dA is the unit area of the substrate at a distance r from the source along the vapor direction (Fig.2) then the amount of material deposited on to the substrate will also depend on  $\theta$  and the expression (1) and (2) then take the forms.

(i) for point source

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$dm = \frac{m}{4\pi r^2}$ . $dA$ , when $\theta = 0$	(3a)
$dm = \frac{m}{4\pi r^2} \cdot cos\theta dA$ , when $\theta \neq 0$	(3b)

(ii) for a source surface

т

$$dm = \frac{m}{\pi r^2} \cdot \cos\psi dA$$
, when  $\theta = 0$  (4a)

$$dm = \frac{m}{\pi r^2} \cdot \cos\psi \cos\theta dA$$
, when  $\theta \neq 0$  (4b)



Fig.2 A general configuration of the evaporation source o and the substrate A,  $\psi \& \theta$  are the angles subtended by the normal to the vapor source and substrate surface respectively to vapor direction, d $\omega$  being the solid angle through which the mass evaporates and r is the distance between the vapor source and the substrate, dA being the unit area of the substrate.

The above relation means that the substrate will receive a maximum amount of deposits when  $\theta$ or  $\psi$  or both will be zero. Hence the positioning of the substrate with respect to the source as well as the nature of the source considerably affects the film thickness. If  $\rho$  is the density of the

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material evaporated and t is the thickness, then Eqs. (3a-4b) can be replaced respectively by the following expressions,

For (i) when $\theta=0$	
$t = m/4\pi\rho r^2$	(5a)
When $\theta \neq 0$	
$t = \frac{m}{4\pi\rho r^2}\cos\theta$	(5b)
For (ii) when $\theta=0$	
$t = \frac{m}{4\pi\rho r^2}\cos\psi$	(6a)
When θ≠0	
$t = \frac{m}{4\pi\rho r^2}\cos\psi\cos\theta$	(6b)

Let us now consider the thickness variation of the deposits at different points on the horizontal plane PQRS which is at a distance h from the source. If x is the distance of any point under consideration from the position where the source normal meets plane (Fig. 3) and if the film thickness at two points A & B be to & t, respectively, then for a point source we have

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Fig. 3 configuration illustrates any arbitrary position (B) and the source normal position (A) lying in a horizontal plane of a substrate (PQRS) separated by a distance (X); h & r the distance of A & B from the source O,  $\psi$  being angle subtended by the normal to the vapor source O to the vapour direction OB.

$$t_{0} = \frac{m}{4\pi\rho} \cdot 1/h^{2} \rightarrow (7a)$$
  
$$t_{1} = \frac{m}{4\pi\rho h^{2} \left[1 + \left(\frac{x}{h}\right)^{2}\right]^{3/2}} \rightarrow (7b)$$
  
$$t_{1}/t_{0} = \left[1 + \left(\frac{x}{h}\right)^{2}\right]^{3/2}$$

where  $\cos\theta = h/r$  and  $r^2 = h^2 + x^2 \rightarrow (8a)$ 

for a surface, we have

$$t_0 = \frac{m}{\pi \rho} \cdot \frac{1}{h^2}$$
,  $t_1 = \frac{mh^2}{\pi \rho (h^2 + x^2)^2} \rightarrow (8b)$ 

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$$mh2/\pi\rho h4(1+\frac{x^2}{h^2})2 = mh2/\pi\rho h2(1+\frac{x^2}{h^2})2$$
$$t_1/t_{0=}\left[1+\left(\frac{x}{h}\right)2\right]-2$$

Where  $\cos\theta = \cos\psi = h/r$ .

In the thermal deposition method, vacuum and should be as high as possible i.e the residual vapour pressure should be very low and preferably below  $10^{-5}$  torr or even lower. The evaporant stream of molecules will then have a large mean path and strike the substrate without any significant loss of their kinetic energy due to the collisions of residual gas molecules.

The residual but very low pressure in the vacuum chamber also ensures the non formation of any oxide layer during the evaporation of metals and alloys. If the vacuum is poor i.e when the residual air pressure is not low, then the deposits are likely to be contaminated with some oxides formed during the deposition process and often become blackish and powered and non adherent to the substrate.

A high substrate temperature generally improves the physical characteristics of the deposited films by importing greater mobility to the vapor molecules or atoms condensing over the substrate for migration over the surface.

Uniformity of the deposit thickness over the substrate surface is generally achieved by placing the substrate at an appropriate distance from the evaporant source and also rotating it either around its axis or that of the source or both as the case may be.

### **RESISTANCE HEATING**

### **Thermal evaporation**

Refractory metals like tungsten, molybdenum or tantalum are generally used in the form of wire or strip having different shapes. The choice of particular refractor metal as a heating source depends on the material to be evaporated so that the evaporant material does not react with the refractory metal at the high temperature of evaporation however, the formation of alloy with the source cannot always be avoided. Hence a coating of refractory oxides such as Al<sub>2</sub>O<sub>3</sub>,

BeO or other suitable materials is often given over the filament or strip so as to prevent a direct contact between the molten charge and the refractory metal. In any case, when a direct heating of the charge is made, the filament or strip is precleaned by passing a heavy current through it so as fox a binary alloy partial pressure of the constituent component may be assumed to follow Raouts law for dilute solutions i.e the vapor pressure of each component is depressed compare to that of the pure state by an amount proportional to its concentration. Equation denoting the rate of evaporation of pure element may also be extended to the binary alloys.

Thus for two pure elements A and B the rates of evaporation at a temperature T and with partial vapour pressures  $P_A$  and  $P_B$  may be denoted as  $E_A$  and  $E_B$  respectively.

If MA and MB are the molecules weights of A and B, then the ratio of the rates deposition of the two will be

$$\frac{EA}{EB} = \left[\frac{PA}{PB}\right] \left[\frac{MA}{MB}\right]^{1/2}$$
(9a)

Assuming that Raoult's law of depression of vapor pressure is valid for the binary alloy system A B, then according to Holland , the ratio of evaporation of two components A and B from the alloy, will be

$$\frac{EA}{EB} = \frac{WA}{WB} \cdot \left[ \frac{PA}{PB} \frac{\sqrt{MB}}{MA} \right]$$
(9b)

Where  $W_A$  and  $W_B$  are the weight concentration S of the two components A and B in the binary alloy AB. If it is assumed that the sticking coefficient of the two components are the same ,then  $E_A/E_B$  ratio will also represent the deposit composition of the alloy on the substrate. It is thus seen that the composition depends not only on the initial alloy composition but also on the factor the parenthesis in eq 1b and less the later is unity which is not usually so , the deposit composition will not fallow the bulk alloy composition i.e  $W_A, W_B$ . A typical case of the variation of deposit composition is a alloy, say of composition 80: 20 Nickel and Chromium. A continuous vacuum evaporation of the above metals leads to film initially of composition 70:30 and later 50 : 50 to make it white hot for a very short period so that all the surface impurities to the filament or the strip are removed by evaporation and the process is called flash cleaning.

After the above cleaning of the filament, strip or boat whatever may be the form of the evaporating source a little amount the charge is then put into it and a current is slowly passed through the source and gradually increased so that the melt forms a layer over the heating source. Usually a shutter is placed in between the heating source and the substrate so that no vapor stream of the charge can reach the substrate.

When appropriate deposition conditions are established, ie, vacuum filament and substrate temperature, source to substrate distance inclination etc... the shutter is then removed out of the line of vapor stream of the charge in vacuum and the substrate starts,

In the required film thickness is obtained. This is again brought into the original position in vacuum so as to put of further deposition on the substrate and the heating of the filament is then gradually stopped.

In the charge consist of two or more constituents which have different vapor pressures, then the one having higher vapor pressure will tent to vaporize at lower temperate than the other. This happens in ay alloy systems. This means the composition of the vapor stream of the charger will different from that of the charge itself. And when condensed the deposit will have different deposition even assuming the condensation rate is the same for all the constituent species further in addition to the vapor pressure that the evaporation rate of species depends on its molecular weight, temperature etc...,

### **FLASH EVAPORATION**

This method is generally adopted when a material has a tendency to decompose or dissociate during evaporation as in the case of some alloys, Group III and V compounds such as indium InSb, AlSb etc... Titanates, Molybdates, even some oxides of metals, etc...,

Basically the process is similar to the thermal evaporation techniques with the difference that only small amount of the charge in powder form is fed at a time to a white hot boat of W, Mo, or Ta takes place without leaving any residue.

Because of the high temperature of the boat as well as the limited amount of the charge fed at a time to the boat there will be no time for the constituent to build by differential vapor pressure.

Hence the composition of the gaseous phase will be more or less the same as that of the charge and it is expected that no condensation of the deposits will be retain the composition of the evaporant. This method of deposition is called flash evaporation, since there is no accommodation of the charge and the heated boat before the arrival of the next charge. The charge in powder form is fed from a reservoir or a hopper to the heated boat through a chute and the feeding rate can be made continuous by using vibrator or suitable cam arrangement.

All other requirements for deposition are more or less similar to those of the normal evaporation process for some oxides are Titanates often a part of the then constantly fed by a small amount of flash charge. Depending on the rate of evaporation by this method a constant composition film can be produced.

### **ELECTRON BEAM METHOD**

This is one of the best method for the deposit of metals, alloys refractory metal etc., as high rate and is now routinely used for the production of the metal film resistor and others.

Multi-electron beam source are also used for special applications.

In this technique an electron beam accelerator with a voltage of say 2 - 10kv is focused on the surface of charge which is normally kept inside a graphite crucible placed on a water cooled upper block (Copper block).

The high energy electron beam emitting form the cathode impinge on the charge as the same potentials the anode converted into intense heat energy which melts the charge.

By suitably focusing the electron beam and controlling its intensity it is possible to heat the top surface of the charge in a mountain condition from which evaporation can take place. As a result a fresh surface id=s exposed every time for further melting and evaporation.

Hence a deposit of more or less of a constant composition is obtained. The temperature attained by the charger at the surface can be as high as above 3000<sup>o</sup>C or by this method and hence refractory metals such as W, Mo, Ta etc can be melted and evaporated by this technique.

There are three types of electron beam guns (Fig. 4)

- A. Work accelerated gun where electron beam coming out of a loop type of a filament. It is accelerated directly towards the charge or through an appropriate shield thus concentrating the beam
- B. Self accelerated gun where the electrons are emitted from hair pin type of filament and focused through a Wehnelt cylinder on the material.
- C. Bent beam electron gun, where a beam of electrons is bent by an appropriate magnetic field, and then focused on the charge.



Fig. 4 Electron Beam method

# **CATHODIC SPUTTERING**

The deposition of metal films by sputtering from a cathode by the glow discharge method was first observed by grove.

The sputtering phenomena is the ejection of atoms from the cathode surface by impinging of energetic positive ions of noble gases such as helium, Ar, Ne, Kr at a reduced pressure under a high dc voltage.

By this technique, it is possible to make various resistive, semiconducting, superconducting and magnetic films.

If the process does not involve any chemical reaction between the bombarding gas ions and the cathode it is knows as physical sputtering.

If on the other hand, some reaction are involved then it is termed as reactive sputtering.

Both these types of sputtering are carried out in a comparatively poor vacuum and are known as high pressure sputtering.

The mechanism of the process involves a momentum transfer between the impinging energetic ions or neutral and the cathode surface atoms as a result of which a physical removal of atoms take place.

The sputtering yields increases with the energy and the mass of the bombarding ions and also with the decreases of angle of incidence to the target.

Sputtered atoms have much higher energies than those of the thermally evaporated one and the former are, however ejected along the crystallographic directions of the cathodes metal lattices.

Sputtering is also accompanied by the emission of secondary electrons from the cathode surface. auger transition also take place along with emission of  $\gamma$  electrons. The sputtering yields is insensitive to the cathode temperature.

According to the sputtering yields can be expressed by the eqn.

 $Y = An^{2/3} E/4Ed[1+[ln (E/Es)/ln2)]^{1/2}]$ 

Where

A= cross section for imparting on energy E greater than Ed which is the energy required for displacing an atom from its place.

E= mean energy of the struck atoms

Es= sublimation

n = number of target atoms per unit volume

 $An^{2/3}$  = number of atoms that each knock hits as it passes through the layer,

For normal cases

 $E_{max} = E >> 2Ed$ 

Sputtered atoms are basically neutral i.e atomic in nature however, a small percentage say about 1% may be in the ionized state. Part of the sputtered material may form polyatomic species and complexes but their relative abundance will be quite negligible compared to the number of neutral atoms.

During sputtering some of the atom of the cathode i.e the targets are likely to be displaced due to the impact of the energetic positive ions to new positions in the lattice and surface migration of atoms may also occur.

If the ions are heavy and have K.E then the target may also be damaged due to their impact.

### GLOW DISCHARGE SPUTTERING

This is the simplest method of sputtering this can be understood from the behavior of gases at reduced pressures under a high dc voltage source.

Conduction through a gas is not generally possible unless a high dc voltage is applied between two electrodes with a gas or air in between them,

A current (ionization current) can pass through the gas or air only when a breakdown of gas or air molecules occurs resulting in their ionization.

The minimum voltage at which breakdown takes place is called breakdown voltage  $v_0$ . This however, decreases with the lowering of the gas pressure. Conduction through a gas at a reduced pressure under an increasing dc voltage gives rise to several electrical and visual phenomena. If the gas pressure is reduce beyond a certain stage that is when vacuum is very high the breakdown of gas and its ionization becomes increasingly difficult.

Soon after,  $v_b$  instead of decreasing, increase with the lowering of gas pressure that is with the increase of vacuum and at a very high vacuum ionization of gas may not take place even at a considerable high voltage such as 30 keV or more.

Our primary concern is for the region where the  $v_b$  decrease with the reduction of gas pressure. voltage –current or ionizations characteristics between two electrodes at a reduced gas pressure under a dc power are illustrated in figure 2.the graph shows several regions as indicated by

numerals 1 to 10 and of this regions 6 and 7 are relevant for sputtering especially the last one for continuous deposition.

Further the current increase is negligibly small with the rise of voltage in the initial stage (1&2) until a minimum voltage is indicated by the dotted line 10 known as breakdown voltage ( $v_b$ ) reached.

It is then followed by a large increase in current a constant voltage continuous with  $v_b$  in the Townsend region (3).

The graph then shows a sharp fall of voltage with the increase of current (region 4&5).it is then followed region (6) known as normal cathode glow discharge region where a glow appears on the cathode but covering it only partially.

The next region (7) where there is a large increase in voltage as well as current is called the abnormal glow region. In this case the cathode is fully covered by the glow. A continuous sputtering can take place only in this region.

The luminous glows in region 6 &7 are self supporting due to the ejection of secondary ( $\gamma$ ) electrons from the cathode by the impact of positive ions. Subsequent regions 8 & 9 are of little importance for sputtering.

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Fig. 5 voltage –current characteristics of a gas at a reduced pressure in a discharge tube with numerals indicating different region of the I-V cure.

- 1. random burst.
- 2. photo electric current.
- 3. townsend discharge.
- 4 . corona.
- 5. subnormal glow
- 6. normal glow discharge
- 7. abnormal glow discharge
- 8. transition region 9.arc discharge

10.breakdown voltage (v<sub>b</sub>) corresponding to Townsend discharge.

Luminous normal & abnormal glow discharge shows some broad visual features namely bright & dark region such the details of which may vary with factors such as gas pressure cathode shape etc (Fig.4).

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Fig. 6 shows the schematic diagram of different region in a glow discharge column;(i) cathode glow (ii) Crookes dark space (iii) negative glow (iv) faraday dark space (v) positive column (vi) anode glow ; Fig.3b. Corresponding voltage drop at different regions along the column.

These consist of (i)-(vi) as one goes from the cathode to the anode.

Luminosity of the negative glow (iii) is the most intense and the next in order comes the positive column (v).if the inter electrode distance is increased or decreased some of above region may increase or decrease and the latter in some case may even merge together .the voltage fall across these gaseous column between the two electrodes it s not uniform and maximum occurs at the cathode dark region (ii) (Fig.3b).

An electron emitted from the cathode under a dc high voltage whist passing through the cathode dark space acquires high energy. Because of a high voltage fall and moves to the edge of the negative glow region.

Different phenomena appearing in a discharge tube at a reduced pressure can broadly be understood from the following consideration viz. (a) Ionization occurs by collision

(b) Only excited atoms or molecules emits light but not moving electrons

above high energy electrons then make collision with gas molecules and ionize them releasing can electron from each collision till it loses its energy to a state which is inadequate for the ionization. Thus in this region considerable number of positive ion-electron pairs are generated these ionized (or excited) molecules emit light giving rise to the negative glow (iii).

The positive ions resulting from such collisions tend to slow down the electrons and the latter in turn lose their power to ionize the gaseous molecules and accumulate thus forming a negatively space charged regions beyond the negative glow region (i.e iii) known as Faraday dark space (iv).

Electron being light, however, move towards the anode under the positive field, acquired sufficient energy and begin to ionize gaseous molecules in the region corresponding to positive column (V).

Positively charged ions formed in the negative glow space region (III) move through it to the cathode dark space (II) by diffusion and are then accelerated to the cathode and strike its surface with a voltage nearly equal to the full voltage drop.

This results in the sputtering of the cathode material as well as the emission of secondary electrons which maintain the glow discharge.

Because of the heavy mass of the ions (+ve) and their high moment, their impact will cause a displacement of atom in the cathode and a consequent damage of the target.

Since the length of the dark and the luminous regions are dependent on various factor viz, gas pressure anode to cathode distance, voltage etc..

The study of the basic process is difficult in a simple discharge tube. However, with the insertion of the third electrode and making it more negative with respect to the anode ie, a second cathode known as the Langmuir's probe the basic process has been investigated in detailed by applying different negative voltages at the new cathode.

Thus at equilibrium the ion current density (J) due to the plasma is given by Langmuir space charge equation.

 $J = (V^{3/2}/t^2)(4\epsilon_0/q)(2e/m)^{1/2}$ 

Where, 'V' is the voltage difference between the target and plasma, 't' is the thickness of the sheath ie, the dark cathode space, ' $\varepsilon_{0}$ ' is the permittivity of the free space, 'e' is the electronic charge and 'm' is the mass of the ions.

For parallel plate electrodes eq. 1a can be written as

$$J = ((2.325*10^{-6})/t^2)V^{3/2} \text{ amp/cm}^2$$
(8b)

Further the ion current J is related to the density of the ions  $(n^+)$  in the plasma ie, the number of ions per unit volume in the plasma by the equation

 $J = (1/4)n^+ \acute{v}e \text{ or } J/e = (1/4) n^+ \acute{v}$ 

Where, 'J' is the average drift velocity of the plasma ions. In a similar way the phenomenon occurring at the anode region can be studied by making the additional electrode more positive with respect to the anode.

The composition for the sputtered film generally confirms to that of the cathode material and the deposition is due to momentum transfer between the impinging ions and the cathode material.

Since process does not depend on temperature and as there is practically no mass transfer, the sputtered material will be of the same composition on as that of the target.

The order to have an ion beam under a high voltage (1-10kv) the pressure of the chamber should be about  $10^{-1}$  to  $10^{-3}$ torr under the action of the acceleration potential of electron the gas inside of the chamber gets ionized. And depending on the voltage between the two electrodes the positives ions flow towards the cathode.

In the normal sputtering method inert gases such as helium, neon, etc. are used for ionization & subsequent sputtering of the cathode.

This is achieved by evacuating the chamber initially to about  $10^{-3}$  to  $10^{-6}$  torr & then passing a purified inert gas through a needle value at a controlled rate so that the chamber pressure increase to a range of  $10^{-1}$  to  $10^{-3}$  torr required for sputtering.

(8a)

The cathode which is at a high negative voltage is generally water cooled & the shape is usually in the form of a disc. The base plate which is generally at the ground potential forms the anode .substrate placed over the base plate are .also at the ground potential.

Sputtering deposition rates are lower than the thermal method & often less than 2000Å per minute.

Material-metals, alloys, semiconductors or dielectrics

# ADVANTAGE

Simplicity, high sputtering rates, deposition of film of uniform thickness & of uniform physical properties.

# DISADVANTAGE

Lower efficiency of sputtering of higher ionization rate, structural inconsistencies of deposits.

# LOW PRESSURE SPUTTERING

Sputtering at lower pressure known as low pressure sputtering normally carried out at or below  $10^{-3}$  torr gas pressure and in some cases as low as  $10^{-6}$  to  $10^{-7}$  torr. It is difficult to ionize the residual gas molecules below  $10^{-2}$ torr. Since the rate of collision of gas decreases with the reduction of pressure. The ionization can, however be achieved simply by increasing the number of electrons for ionization by inserting a second cathode in the system or by increasing the effective free path length of ionizing electrons by the use of crossed magnetic electron fields as in penning discharge system.

In the former case a secondary hot electron gun is introduced to increase the total concentration of ionizing electrons and the process is further enhanced by the presence of a magnetic field inclined to the lines force between the cathode and anode.

In such cases the gas pressure is about one order less than for the normal sputtering and magnetic field is also less. The advantages of system are that a fine control of sputtering rate can be made by adjusting the magnetic field. In the later case ionization is increased by increasing the number of collisions of the residual gas with ionizing electrons.

With appropriate shapes of cathodes and suitable magnetic field say in the form of two solenoids in opposition, a high rate of deposition can be made at pressure of about  $10^{-5}$  torr. In a

third method low pressure sputtering is carried out by the use of radio frequency of several order mega hertz.

# **REACTIVE SPUTTERING**

During sputtering it is also possible that under certain condition the target material may react with the ionized gaseous species in the chamber.

If the gases like oxygen or nitrogen are used a media, the ionized species derived from them can react with the target to form oxide or nitride films.

Oxides film such as CuO, CoO, NiO etc. have been obtained from hot taints. Nitrides, borides and many other films which cannot be easily. Prepared by other techniques can be easily. In appears that the sputtered material during its flight from the tayets to the substrates reacts with the ionized nitrogen or boron or other species.

These reactions are quite vigorous and film of reacted materials is deposited on the substrate surface. It is also possible to form films of mixed nitrates, borides etc... if the target is made of some suitable composition and an appropriate gaseous atmosphere is maintained in the sputtered chamber, then different types of films of mixed compositions can be prepared comparatively easily.

## **R.F.Sputtering**

Unit – I Nature of Thin Films

R	matching Torget Plasma
	Bubstrate 1
	- 7 Ford Pross well.

Fig. 6 R.F. Sputtering configuration

Enhanced ionisation can be achieved in the R.F field so that sputtering can be done at pressure lower than that of ordinary glow discharge.

With a low frequency A.C field between two electrodes of a discharge tube, there will not be any ionisation of gases since both the electrodes will have alternate polarities.

With increasing frequencies say in the range between 100KHz to about a few MHz there will be sustained glow discharge due to the ionisation of gases by the oscillating electrons of high frequency field and not by the secondary electron as in the case of D.C discharges.

These electrons gain energy from the field and move in the different directions and hence do not require any high field. These plasma electrons also acquire same positive voltage with respect to the electrodes.

This technique of particularly useful for the deposition of dielectric materials since in D.C sputtering some of the charges also build upon the dielectric material target. Surface as a result of which sputtering efficiency goes down.

This can be derived by using the R.F. method ie, by applying a high frequency potential (MHz range) to the gaseous plasma.

### Chemical vapor deposition or vapor plating;

The deposition of films from gaseous phases by thermal decompositions (pyrolysis) or chemical reactions on substrate surfaces at high temperature is known as the chemical vapor deposition process (CVD) or vapor plating.

This technique is used for the preparation on various inorganic as well as organic compounds

The basic principles involves decompositions or partial dissociations of the vapor phase species and their subsequence deposition on substrate or reactions amongst the vapor species in a neutral atmosphere or otherwise and the deposition of the products.

Sometimes a carrier gas is also introduced either to control the rate of reaction or to prevent undesired reaction at the prevailing elevated temperature.

An appropriate control of the rate of flow of the gaseous species ,temperature & pressure of the reaction chamber loads to the formation of films are as given below

AB decompose  $\rightarrow$  A+B

AB+CD dissociate  $\rightarrow$  AC+BD dissociate

 $2AB_2$  dissociate  $\rightarrow AB_4 + A$  etc

 $(AB)_2$  dissociate  $\rightarrow$  nA+nB

Where A,B,C,D are different constituent and n is an integer.

## THERMAL DECOMPOSITION OR PYROLYSIS

Many halides or organometallic compounds when heated to a high temperature decompose resulting in the formation of solid as well as gaseous phases.

In many cases some secondary gaseous phases also result which can further decomposes to desired solid films.

Thus when organometallic compound of silicon such as tetra ethoxy silane, tetra ethylene ortho silicate etc. which are liquid in form are heated to a temperature of about 700-900°c, a dielectric film of SiO<sub>2</sub> is formed as shown by following equation.

 $Si(OC_2H_5)_{4 \rightarrow}SiO_2{+}4C_2H_4{+}2H_2O$ 

Another example of pyrolytic decomposition is the formation of silicon or germanium from silicon or germane at about 700-900°c at a presence of 10 torr.

The reaction takes place in the following way

 $SiH_4 \rightarrow Si+2H_2$ 

 $GeH_4 \rightarrow Ge+2H_2$ 

Silicon films can also be prepared by the reduction of tetra chloro silane vapour with an alkali metal hydride in the presence of an organic solvent such as tetra ethylene glycol dimethyl ether and dissociation of the product namely silane as expressed b the equations.

SiCl<sub>4</sub>+LiAlH<sub>4</sub>→SiH<sub>4</sub>+LiCl+AlCl<sub>3</sub>

 $SiH_4 \rightarrow Si+2H_2$ 

A compose process of pyrolysis is the preparation of corban resistors by passing benzene or toluenevapours at a temperature between 800-1000°c as shown by the equation.

C6 or C6H5CH3 $\rightarrow$ C+ gaseous products

# VAPOR PHASE REACTION

Constituent species in the gaseous phase react in the presence of inert, oxidizing or even some reducing atmosphere to form the desired product. Thus SiO<sub>2</sub> films can be produced by the reaction of SiCl<sub>4</sub> vapors with carbon dioxide in the presence of hydrogen gas

 $SiCl_4+CO_2+H_2 \rightarrow SiO_2+CCl_4+H_2$ 

 $SnO_2$  films often used as metal oxide resistors can be prepared from  $SnCl_4$  vapors in presence of water and HCL vapors at a temperature about 500°c and the reaction can be represented by the equation

 $SnCl_4+2H_2O+HCL \rightarrow SnO_2+4HCl+HCL$ 

Often chloride vapor of indium, antimony or bismuth are also passed along with those with those tin chloride to produce doped tin oxide films to improve the quality of the film resistors.

# VAPOUR TRANSPORTATION METHOD

In this method vapors of two reacting constituents are passed over the substrate kept at a high temperature region where the reaction take place to form the desired films. This technique is often used for the preparation of very thick films and wafers and even flat shaped crystal of several mm size. in thus technique there will be three temperature zones, two for vaporization of the two constituent elements at two different parts of the system and then bringing than together to react at a third thermal zone to form the desired product.

This process is known as Günter method which has been used for the preparation of single crystal wafers of CdS, CdSe, CdTe and others.

### **Disproportion method**

This depends on the difference in the stability of polyvalent metal compounds at two temperatures.

If the higher valency state compound is more at low temperature and the lower valency one is at a higher temperature then by passing the vapor of the lower valency state compound through a lower temperature range, the following reaction may take place

 $2AB \rightarrow A + AB_4$  at a low temperature range

 $AB_4 \rightarrow AB_2 + B_2$  at a higher

 $AB_4+A \rightarrow 2AB_2$ 

Where A and B are the two constituents. This method is often used for the preparation of high parity silicon and germanium films from  $SiI_2$  and  $GeI_2$  respectively.

Both  $SiI_2$  and  $GeI_2$  are stable at lower temperatures whereas  $SiI_2$  and  $GeI_2$  at comparability higher temperature

By preparing SiI<sub>2</sub> vapors at higher temperature and passing them through a tube kept lower temperature . SiI<sub>2</sub> thus formed can be again be converted to SiI<sub>2</sub> by passing these vapor through a tubular furnace over a highly pure silicon substrate kept at a higher temperature say above  $1100^{\circ}$ c. for the formation of Ge films the two temperatures region of dissociation and formation of iodides. Shown in the above equation will be about 200and 300°c only which are much lower than for silicon iodides.

#### **Chemical deposition**

This method depends on the deposition of films from aqueous solution either by passing a current or by chemical reaction under appropriate conditions and is generally used for the deposition of thick metallic or alloy films.

By the very nature of their preparation conditions there film are not generally of high purity.

Despite this limitation this technique is widely used for the fabrication of conducting connectors, magnetic memory elements.

With an appropriate control the deposition parameter such as bath composition, temperature, pH, current density etc. metallic deposits and even alloys of definite composition can be obtained.

### **Electro deposition**

When a current is passed through a solution of some metal salt between two electrodes of the same or different metals, the deposition of metal from the solution takes place at the cathode surface following the faradays law.

### W=zita

Where w is the weight of the metal deposited, z is the electrochemical equivalent, I is the current passed, t is the time.

Cathode efficiency depends on various factors such as bath composition, pH, temperature, current density etc.

The mechanism of deposition involves the dissociation of metal salts to anions and cations the deposition of their charges to form metallic films.

In electroplating the anode is generally of the same metal which is to be deposited on the cathode.

When some current is passed through the bath solution the amount of metal deposited at the cathode is given by above equation and corresponding amount of metal from the anode goes in to solution.

Electrode reaction for a divalent metal salt bath can be expressed by the following equations.

## $M^{++}+2e- \rightarrow$ at the cathode

 $M \rightarrow M^{++}+2e$  at the anode

Where m is a divalent metal similar types of reactions also take place for mono and trivalent metals.

The dissolution of metal anode to form the metallic salt can be treated as the oxidation process whereas the deposition of metal at the cathode surface as the reduction process.

Thus when a metal is deposited at the cathode an equivalent amount of metal ions should also go into the solution from the anode. If however, the later process does not take place, then a side reaction involving the evolution of oxygen occurs at the anode as given below

### $2H_2O \rightarrow 2O+4H^++4e$ - at anode

And the solution becomes more acidic near the anode region. This oxygen because of its nasect condition is in highly active rate and hence often reacts with the anode material forming an oxides layer over it as given by

### М+О→МО

### $2M+O \rightarrow M_2O$

In the partially deposition process, the bath conditions various constituents, viz metal salts, complexing agents to reduce the metal salt concentration, PH controlling agents, many additionally compound known as leveling, brightening, surface tension reducing agents etc. Hence bath composition, PH, current density has to be suitably controlled to get the desired quality of the deposits.

By an appropriate choice of metal salts and other constituents it is possible to deposit alloys of constant compositions at the cathode either by the constant potential or constant current method.

Anodic oxidation

The reactions indicated by eqn indicate how anodic oxide layer are formed. In order to obtain a good anodic oxide film, the bath composition and the d.c voltage have to be appropriately controlled.

The electrolytes can be alkali or acidic in nature. for the former cases caustic soda, phosphate, tartarate, citrate, etc. the formation of anodic oxide layers takes over the anode and often with simultaneous evolving of oxygen at the cathode instead of metal deposition an equivalent amount of hydrogen is evolved. The formation of oxide layers at the anode surface is due to the reaction of the nascent oxygen with the anode material, nascent oxygen being formed by the dissociation of under dc potential.

The reaction at the two electrodes can be represented by the following eqns.

 $M+H_2O \rightarrow MO+2H^++2e^-$  at anode

 $H_2O+2e-\rightarrow H_2+2(OH)$ - at cathode

The thickness of the anodic oxide layer generally increases with the passages of current. The physical characteristics of the anodic oxide layer depend not only on the compositions of the electrolytes but also on the temperature, PH, as well as the impressed voltage.

Dielectric oxides films of Al<sub>2</sub>O<sub>3</sub>, Ta<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>U<sub>5</sub> etc on Al,Ta,Nb formed by anodic oxidation method are now largely used as capacitor elements for industrial applications.

The impressed voltage in the individual cases for oxides formation may vary widely between 0 to 500 v depending on the types of capacitors, their grade, bath composition etc. and the film thickness may be between 1 to 10 microns.

## **Electroless plating**

In this process metal films can be deposited without passing any current and the film thickness can be built up to an order of micron or more the substrate can be both metals and non conductors.

Advantages

1. Uniform deposition can be made even to intricate parts and deep recesses of any design where the normal electro-deposition method may not be suitable.

2. This is now being used for the preparation of specialized films required for electronic and other process.

This process originally developed by Brenner and riddle was suitable only for some metals like nickel, platinum etc but not for so called inactive metals such as brass, copper, lead etc... The original process was later on modified and now a days not only inactive metals but also non conductors can be coated by electroless plating technique with the help of suitable sensitizing and activated solution treatments.

The basic principle of this process is the reduction of a metal salt on a substrate surface by a reducing agent and once on initial coating is formed, further of nickel and cobalt along with varying amount of phosphorous as phosphides such alloy films are now being used as magnetic memories. It is also possible to deposit precious metal films by this process.

Film thickness and its control

Thickness plays an important role in the film properties unlike a bulk material. In many applications, particularly so in the case of optical device such interference filters, antireflection coating, etc. the success of the fabrication depends only on the deposition of specific thickness of the dielectric layers.

A good control of specific thickness will still be essential.

In all thickness measurements it is generally assumed that these films are homogeneous and more or less uniformly deposited on the substrate so that there will be have a mean thickness. However, when films are thin i.e their thickness are law say less than about 500Å and specially in the cases of ultra thin films, the deposit layers will be discontinuous and non uniform and maybe intersperse with voids or pinholes. In such cases a mean film thickness may not have any significant at all since d at any specific area, may vary from o to any value much higher than the so called mean film thickness. It only indicates the likely magnitude of the film thickness. If the deposition is carried out in a controlled condition then mean d or t will be close to the film thickness at any placed over the substrate surface.

Deposition can go auto catalytically. The reducing agent normally used is sodium hypophosphite through recently borohydrides and azides are also being used the mechanism of nickel deposition with sodium hypophosphite can roughly be represented by the following expression

 $Ni^{++}+H_2PO-+H_2O \rightarrow Ni+H_2PO_3+2H^+ \rightarrow (1a)$ 

## $H_2PO_2+H_2O \rightarrow H_2PO_3-+H_2 \rightarrow (1b)$

and the metal deposition is accompanied by evolution of hydrogen as shown by Eqn 1b. the above reactions go on smoothly but vigorously  $>80^{\circ}$ c. in the above reactions some metal phosphides with varying phosphorous content in the film say between 3-12% or even more depending on the bath composition, temperature and Ph are also formed. the metal deposition can be carried out both in acidic and alkali solution and the rate of deposition depends mostly on the bath composition and temperature of the solutions, reducing agents using borohydrates, hydrazine etc lead to the formation of boride and nitride films.

### Advantages

It is possible to coat even non conducting materials such as glass, ceramics, polymers, with metal films. Substrates have to be first sensitized and then activated or bath the treatments can be carried out simultaneously. The treated substrates after thorough washing are dipped into the electroless plating solution at an appropriate temperature and the deposition takes place. Further film growth takes place auto catalytically. Instead of using a single salt often a mixture of metal salts such as nickel and cobalt are used and the deposits will then consists of an alloy film thickness measurements techniques are based on different principles such as the mass difference, light absorption, interference effect, conductivity, capacitance etc of the films with increasing thickness. These measurements can be either in a dynamic or static condition. In the former d or t is measured during the deposition process whilst in the latter after its completion.

### MASS METHODS

# MICROBALANCE TECHNIQUE

This methods depends on the increase of the weight of a film due to its mass increase and from the knowledge of its density and the deposited area, film thickness (d or t) can be evaluated from the relation.
Unit – I Nature of Thin Films

d or t = $W/\rho A$ 



Fig.1(a) quartz fiber type microbalance



Fig.1(b) torsion fiber suspension and electromagnetic force compensation type balance

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#### Unit – I Nature of Thin Films

Where W is the weight difference of the film,  $\rho$  density and A is the deposited area. The increase in the film weight can be measured by a suitable micro balance. The above technique with appropriate modifications as in a quartz fiber microbalance can be used as a rate monitoring system also.

This balance is mode of quartz and the deposits are formed on a pan which is suspected from the end of a beam by means of a quartz fibre, the other end carrying a counter poise. A pointer or a mirror is attached to the beam of the balance.

With the increase of weight of the film the pointer moves and its displacement with reference to a fixed point can be measured with a telescope and in the case of a mirror by means of a lamp and scale arrangement. The movement of the pointer can be standardized against known weights. Alternatively, the balance can be modified in such a way that the deflected beam can be brought back to its original position by a suitable magnet and a solenoid coil through which an appropriate current is passed, the change in current being proportional to the increase in the weight of the deposit.

In other variation of the technique a quartz spring with a pan attached to it is used. An increase in weight of the film will extend the spring and the elongation will be proportional to the mass deposited.

This system can be used both as a thickness meter as well as a monitoring system. The sensitive of a microbalance is the order of  $10^{-7}$  to  $10^{-8}$  g and can be improved further.

#### **CRYSTAL OSCILLATOR:**

This method was first investigated by Suerbreg and later on Lostis and others.

In this method thickness measurement depends on the oscillation of a quartz crystal when excited and the frequency of its oscillation depends on its thickness as given by the relation F = (1/2t) = N/t (mm kc/sec) (1a)

#### Where

'f' is the frequency of the crystal, v is the velocity of the elastic transverse waves normal to the crystal plate, t is the thickness of the crystal and N is the frequency constant depending on the nature of the crystal.

For the AT- cut quartz crystal ie, at an angle 35<sup>0</sup> 20' the value of N =  $(c/4 \rho_q)^{1/2}$  = 1670mm kc/sec, where  $\rho_q$  is the density of the crystal and C is its shear elastic constant.

The above equation on differentiation with respect to thickness t and replacing thickness by mass leads to the expression.

 $Df = -(f^2 dm/N \ \rho_q A) = -C_{f0} dm/A = -C_f t \ \rho_{flim} \eqno(1b)$  Where

 $Cf_0 = f_0/N \rho_q$ ) in g/cm<sup>2</sup>, dm(A.t,  $\rho_{flim}$  is the increase in mass due to the deposition of film, df is the frequency difference,  $\rho_{flim}$  is the density of the film and A is the area of the deposit. The negative sign in equation 1b indicates a decrease int e frequency with the increase in film thickness. Hence from eq 1b, we have

 $T = - df / C_{f0}. \rho_{flim}$ (1c)

From the above relations film thickness t can be measured. It is also seen that the change of frequency is due to the change in mass due to the deposition of a film on the quartz surface.

In the above it has been assumed that the front face of the quartz crystal acts as the antinodal point of the transverse wave and also that the film thickness has no effect on to the elastic constants of the crystal. The latter, however, may not be true for all thickness ranges. The term  $Cf_0$  is called the sensitivity for mass determination.

The assumption that the change in the frequency is proportional to0 the weight increase may not also be true for all cases and in fact with the increase of film thickness, the variation may depart from the linear relation (Eq 1c)

Further with the change of temperature, the temperature coefficient of frequency may also change. In that case the above relations may not hold good. However, an AT-Cut quartz crystal has the minimum temperature coefficient of frequency (TCF). To compensate the temperature effect the crystal is generally cooled so that there is no appreciable rise in the temperature of the quartz crystal during the deposition of films or during measurements.

A circular shaped mental electrode is deposited on the central area of each face of the quartz crystal which is kept in a box, the latter being in contact with a cooling block. The box has an opening through which the vapor stream may come and deposit on the electrodes of the

crystal. The sensitivity of a quartz thickness meter or monitor is about  $10^{-8}$ g/cm<sup>2</sup>. This equipment with an appropriate modification of its circuit can also be used as a rate monitoring system.

**Nature of Thin Films** 

#### DEPARTMENT OF PHYSICS MSC PHYSICS (2017-2019) MATERIAL SCIENCE(17PHP105A) 2017-2018 (ODD) MULTIPLE CHOICE QUESTIONS

#### Unit-I

QUESTIONS	Option 1	Option 2	Option 3	Option 4	Answer
Thin film may be arbitrarily defined as a solid layer having a thickness varying from a few Å to about	10mm	10cm	10µm	10^-3 nm	10µm
Thickness of ultra thin film is	>1000Å	50-100Å	100-1000Å	none of these	50-100Å
An ideal film extended infinitly in directions but restricted along	two and z direction	one and z direction	three and none	none of these	two and z direction
Highly conducting Na, K,Au and Pt etc in the bulk form show -ve TCR when in thin film states thus behaving as	semiconductors	conductors	insulators	dielectrics	semiconductors
A freshly formed film surface becomes highly reactive due to	high volume to surface ratio	high surface to volume ratio	high thickness	none of these	high surface to volume ratio
Characteristic of a surface are more often observed in	amorphous	single crystal	polycrystalline	thin films	thin films
Thin films can be prepared from a variety of materials such as	metals	semiconductors	insulators	all the above	all the above
The primary requirement for the methods (a) Thermal deposition and Sputtering is a	high vacuum	higher than ambient pressure	ambient pressure	none of these	high vacuum
involves the evaporation or sublimation of the material in vacuo by thermal energy	sputtering	CVD	Thermal deposition	chemical deposition	Thermal deposition
When all the molecules are condensed, sticking coefficient has a max. value of	100	1	10	1000	1
When none is deposited, sticking coefficient has a min. value of	1	10	0	-1	0
velocity distribution of evaporant molecules will depend on the	nature of the source	nature of the substrate	nature of the target	none of these	nature of the source
The emitted vapour stream will have the same velocity distribution in all directions thus resembling the emission from	surface source	point source	cylindrical source	prism source	point source
For,the emission velocity of the vapour stream will decrease with the increase of the angle of inclination	point source	surface source	cylindrical source	none of these	surface source

If $\Psi=0$ , then a surface source resembles a	cylindrical source	point source	cylindrical as well as point source	none of these	point source
Heating sources are made from	refractory metals	semiconductors	insulators	none of these	refractory metals
The amount of deposits received by a substrate will depend not only on the nature of the source but also on the inclination of the vapour stream with the	substrate-normal direction	source-normal direction	source as well as substrate normal	none of these	substrate-normal direction
Positioning of the substrate with respect to the source as well as the nature of the source considerably affects the	film growth	film thickness	film purity	none of these	film thickness
A highgenerally improves the physical characteristics of the deposited films	source temperature	substrate temperature	nature of the substrate	substrate thickness	substrate temperature
Higher vapour pressure constituent will tend to vaporise at a	lower temperature	higher temperature	lower as well as higher temperature	none of these	lower temperature
There is no accumulation of the charge on the heated boat in	Thermal evaporation	Electron beam method	sputtering	Flash evaporation	Flash evaporation
Which method is generally adopted when a material has a tendency to decompose or dissociate during evaporation	Flash evaporation	Electron beam method	sputtering	CVD	Flash evaporation
A constant composition film can be produced by	Electron beam method	sputtering	Flash evaporation	CVD	Flash evaporation
In which method several sources are simultaneously used for the evaporation of the constituent species	multi evaporation process	Electron beam method	sputtering	evaporation process	multi evaporation process
The simultaneous deposition process from different sources is known as	co-evaporation	multi evaporation process	evaporation process	Electron beam method	co-evaporation
In electron beam method the electron beam is accelerated withvoltage	2V	4kV	10V	2-10kV	2-10kV
Which method is now routinely used for the production of metal film resistors and others	Electron beam method	multi evaporation process	sputtering	Flash evaporation	Electron beam method
There aretypes of electron beam guns	three	two	one	five	three
In, electrons are emitted from hair pin type of filament	work accelerated gun	self-accelerated gun	bent beam electron gun	none of these	self-accelerated gun
In Electron beam is bent by an appropriate magnetic field	work accelerated gun	self-accelerated gun	bent beam electron gun	none of these	bent beam electron gun
The deposition of metal films by sputtering from a cathode by the glow discharge method was first observed by	Wehner	buckel and hilsch	grove	pease	grove

Sputtering yield increases with the of the bombarding ions	mass	energy	mass and energy	none of these	mass and energy
Auger transition takes place along with emission of	α-electrons	β-electrons	γ-electrons	radiation less	γ-electrons
If the process does not involve any chemical reaction between bombarding gas ions and the cathode is known as	reactive sputtering	physical sputtering	high pressure sputtering	both b and c	both b and c
If the process involve any chemical reaction between bombarding gas ions and the cathode is known as	reactive sputtering	physical sputtering	high pressure sputtering	both a and c	both a and c
Glow discharge is used to clean	dirt	plastics	polymers	none of these	dirt
The simplest method of sputtering is by the	glow discharge technique	Electron beam method	Flash evaporation	evaporation process	glow discharge technique
The minimum voltage at which breakdown takes place is called	transition region	abnormal glow discharge	break down voltage	normal glow discharge	break down voltage
In glow discharge sputtering, the region where there is a large increase in voltage as well as current is called the	abnormal glow region	townsend region	normal glow discharge	transition region	abnormal glow region
In glow discharge sputtering, the region where there is a large increase in current at a constant voltage is called the	abnormal glow region	townsend region	normal glow discharge	transition region	townsend region
A continuous sputtering can take place only in	transition region	townsend region	normal glow discharge	abnormal glow region	abnormal glow region
in glow discharge sputtering, luminosity of the is the most intense	cathode glow	negative glow	anode glow	faraday dark space	negative glow
Which technique is particularly suitable for refractory materials whicb caannot easily be deposited by other methods	glow discharge sputtering	Electron beam method	Flash evaporation	evaporation process	glow discharge sputtering
In method, gases like oxygen or nitrogen are used as media	glow discharge sputtering	Electron beam method	Flash evaporation	reactive sputtering	reactive sputtering
Different types of films of mixed compositions can be prepared comparatively easily by	Low pressure sputtering	reactive sputtering	Electron beam method	glow discharge sputtering	reactive sputtering
Enhanced ionisation can be achieved in the	r.f.field	d.c.voltage	reactive sputtering	low pressure sputtering	r.f.field
Sputtering of cathode materials in presence of inert or active gases either at	low pressure	medium pressure	high pressure	all the above	high pressue
In low pressure sputtering, ionisation of gas molecules takes place at low vacuum say	10^-1 torr	10^-15 torr	10^-10 torr	10^-6 torr	10^-1
In RF sputtering method an impedance matching between is necessary	Power supply and electrode	Discharge tube and DC voltage	Power supply and discharge tube	Electrodes and DC voltage	Power supply and discharge tube

RF sputtering technique is particularly useful for the deposition of	Insulator	Dielectrics	Semiconductor	Conductor	Dielectrics
The deposition of films from gaseous phases by thermal decomposition is known as	chemical vapour deposition	sputtering	Thermal deposition	evaporation process	chemical vapour deposition
Which technique is used for the preparation of various inorganic as well as organic compounds	chemical vapour deposition	sputtering	Thermal deposition	evaporation process	chemical vapour deposition
When tetra ethoxy silane is heated to a temperature of about 700-900°C, a dielectric film ofis formed	SiO2	Si	SiH4	С	SiO2
Gunther method has been used for the preparation of wafers of CdS,CdSe etc.	Single crystal	Polycrystal	Amorphous	both a and c	Single crystal
Which method has three temperature zones	Vapour phase reaction	vapour transportation method	Disproportionation method	pyrolysis	vapour transportation method
The SiO2 films can be produced by the reaction of SiCl4 vapours with CO2 in the presence of H2 gas is known as	Gunther method	Philips process	Disproportionation method	pyrolysis	Philips process
Which technique is often used for the preparation of very thick films and wafers and even flat shaped crystals of several mm sizes	Vapour phase reaction	vapour transportation method	Disproportionation method	pyrolysis	vapour transportation method
Which method depends on the difference in the stability of polyvalent metal compounds at two temperatures	Vapour phase reaction	vapour transportation method	Disproportionation method	pyrolysis	Disproportionation method
Which method depends on the deposition of films from aqueous solutions either by passing a current or by chemical reactions	chemical deposition	chemical vapour deposition	evaporation process	sputtering	chemical deposition
In process metal films can be deposited without passing any current	electrodeposition	anodic oxidation	electroless plating	chemical reaction	electroless plating
In mass method balance methods is made of	silica	glass	quartz	magnesium	quartz
In crystal oscillator thickness measurement depends on the oscillation of a	Quartz fibre	Quartz crystal	Quartz amorphous	Quartz film	Quartz crystal
Which method uses interference fringes for the measurement of film thickness?	crystal oscillator	photometric	ellipsometry	interferometry	interferometry
Which of the following technique comes under mass methods	crystal oscillator	photometric	ellipsometry	interferometry	crystal oscillator

Which is a very accurate method which is eminently suitable for measuring the thickness of surface layers or films as well as their optical constants	ellipsometry	interferometry	photometric	microbalance	ellipsometry
Degreasing and cleaning are carried out in a closed chamber by suspending the substrates in vapours of organic solvents such as	carbon tetrachloride	alcohol	trichloro ethylene	both a and c	both a and c

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**Electron Diffraction Technique:** Electron diffraction technique – High energy electron diffraction – Low energy electron diffraction – Electron microscopy – Scanning electron microscopy – X-ray photoelectron spectroscopy – Mass spectroscopy – Thermodynamics of nucleation – Nucleation theories – Film growth – Incorporation of defects, impurities etc. in film – Deposition parameters and grain size.

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#### HIGH ENERGY ELECTRON DIFFRACTION (HEED)

Monochromatic electrons are emitted from a hot or cold cathode under an accelerating field of high voltage say between 60 to 200 keV and pass through an aperture on a diaphragm which works as the anode normally at the earth potential. The body of the instruments is also connected to the earth.

The negatively accelerated electrons beam generated under a highly stabilized power source. Than passes through a magnetic or electrostatic lens for containing the beam and then sickness the specimen surface either at a low glancing incidence or is transmitted through it.

By controlling the lens current both the central and diffracted electron beams can be focused on a florescent screen.

A high vacuum pumping system is used to evaluate the high equipment to about  $10^{-4}$  to  $10^{-6}$ torq.

The design of the specimen holder is such that it can be rotated along an axis moved forward and backward and even titled so as to facility point to point investigation of specimen films by reflection or transmission method.

Fig 1 a schematic diagram of an electron diffraction camera where the electron source diagram position screen etc., are indicated.

A diffraction pattern from a single crystal from a to the reciprocal lattice net word of real crystal lattice magnified lambda L times when recorded on a plate or observed on a screen lambda and L is the distance between the monochromatic beam and L is the distance between the specimen and the photographic plate. In the photographic plate, the spot obtained correspond to different planes of the crystal which fulfil the Bragg reflection condition, constitute with the electron beam diffraction and can be identified from their geometrical disposition and also by measuring  $d_{hkl}$  of each spot provided  $\lambda l$  and lattice parameter are known since the surface of a sphere of reflection for high energy electrons. Hence by indexing and identifying these reciprocal lattice spots crystal lattice spacing can be evaluated from the relation.

 $\lambda L = r1d1 = r2d2 = r3d3....etc$ 

where  $\lambda$  is the wavelength of the monochromatic electron beam and L is the distance between the specimen and the screen r1, r2, r3.... Are respectively the spot distance from the

# undeflected beam spot and d1,d2,d3....etc are the interplanar spacing of different spacing of the different planes of specimen under investigation for an accurate determination of $\lambda L$ which depends on the electron energy. A standard material yielding sharp diffraction spots or rings is used under investigation and diffraction pattern from both of them are simultaneously recorded on the plate. Generally (11230) reflection of graph plate (d = 1.230A<sup>0</sup>) is used as a standard.

The accelerating potential of electrons is about 40-100kev or even more specimens can examined by reflection method and when thin also by transmission technique.

#### LOW ENERGY ELECTRON DIFFRACTION (LEED)

The use of low energy electrons (5-500eV) for studying the surface layers if nickel singe crystal was first made by Davison and Germer.

Slow electrons because of their low energy interact strongly with matter and are completely scattered by the surface atoms. Since the scattering of electrons is also elastic, the surface layer atoms behave as 2D rather than 3D scatterers. The depth of penetration of slow electrons is about a few  $A^0$  compared to about 10-20  $A^0$  for the HEEP.

The diffraction is similar in both case except that the elastically back scattering electrons are utilised for observing the diffraction pattern rather than the transmitted once as in sum HEED cases. Further the vacuum conditions in LEED is much more stringent and an order of  $10^{-9}$ -10— $^{10}$ torq. Is essential for studying the surface layers

The instrument in it basic design consist of an electron emitting source (V shaped W filament ) having negative accelerating voltage of about 5-500 eV (1), a Weinent cylinder (2)and it is followed by a lens systems (3). Electrons after passing through the above strike the crystal surface (4) & the back scattering electron than pass through grids (5,5'). The space between the crystal and the first grid (5) is generally field free, so that the diffracted electrons can go straight lines. The second grid (5<sup>1</sup>) knows as repel is approximately at the same potential as the cathode , so that the in elastically scattered electrons cannot pass through the grid to the florescent screen (6), which is kept at a high positive potential say ...

The diffracted electrons after passing through the repelling grid are further accelerated by the high potential of the florescent screen where the diffraction pattern is observed and it can be recorded. The whole system is evacuated by a high vacuum pump system (7) comprising of a high capacity sorption pump, a getter pump, etc., the crystal (4) can be suitably manipulated to provide rotations, to and few movements or tilt etc. so that the different areas of the crystal surface can be exposed to the impinging slow electrons.

A LEED study concurs primarily about the nature of the surface layer consisting of a few atomic plans, surface contamination, formation of oxide layers, nature of clean surface, etc. since the study involves a change in the surface in the presence of a minute amount of gas or due to adsorption or reactions or reactions in high vacuum the diffraction patterns from the new surface layers thus formed are referred with respect to the initial clean surface.

#### SCANNING ELECTRON MICROSCOPE (SEM)

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This is one of the most useful and versatile instruments for the investigation of surface a topography, micro structural feature, etc .provides a pictorial display of the surface layer with a high depth of focus greater than that possible in a electron microscope thus providing better details than that by the conventional replica technique.



The principals involved in imaging is to make use of the scattered secondary electrons when a finally focused electrons beams images of the surface of the specimens at the point of contact several process may take place by which electrons, photons etc., may be emitted. In SEM the secondary electrons are primarily used these generally have very low energy say <50eV compared to =30kV of the primary electrons and hence only those secondary's which are generated at the surface layers can leave the surface. These secondary are formed by the interaction of the primary electrons beam with the loosely bound electrons of the surface

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atoms and their emission is very much sensitive to the incident beam direction and the topography of the surface atoms and the contrast is primarily due to their factors. The more oblique is the surface the greater will be the surface area from which secondary electron can emit. The contrast hence depends on the rate of the secondary electron yields and the incident angle of the primary beam to the surface element.



Fig. 1 Schematic diagram of SEM

The basic instrument consists of an electron source, a series of lens system to produce a finely focussed electron beam on the specimen surface, two pairs of deflection coils at right angles to each other & connected to a saw tooth wave generator system so that a finely focussed electron beam describes a rectangular zig zag rastes i.e. specimen scanning. The emitted secondary electrons are collected which is amplified & then sed to a cathode ray display tube (CRT). Fig.1.shows a schematic diagram of a SEM. As the electron beam scans the specimen surface there will be a change in the secondary electron emission according to the surface texture. The scanning picture observed on the CRT represents the image of me surface. The winding of the coils in the main body & in the CRT are so adjusted that a magnified image is formed.

# X – Ray photoelectron Spectroscopy (XPES) or Electron Spectroscopy for chemical Analysis (ESCA).

This is a very useful tool for the analysis of surface layer of metals, semi conductors& insulators of thickness about 5 to 25°A & for organic compounds & Polymer materials of thickness about 40 to 100°A. It can be used in a less stringent vacuum conditions compared to the other techniques.

When a specimen is bombarded with the X-ray photon, these are absorbed by the surface atoms resulting in a corresponding emission of photo electrons from the surface atoms. Electrons from all orbitals with a binding energy smaller than that of me X-ray energy all then removed & detected in a spectrometer and the relation is mathematically expressed as

$$Eb = h\gamma - KE + Q \qquad \rightarrow (1)$$

Where  $E_b$  is the binding energy of orbital electrons K.E is the Kinetic energy of photo electrons.  $\gamma$  is the radiation frequency & Q<sub>s</sub> is the spectrometric.  $\gamma$  is the radiation frequency & Q<sub>s</sub> is the spectrometric correction factor. This analysis is carried out by finding out the energy distribution of photo electrons emitted from the surface of the material. The composition of the surface material is readily determined from the position of the peaks in the ESCA electron spectra & the chemical bonding from their positions & the shape of the ESCA peaks. The ESCA technique is now widely used for the analysis of organic materials, especially reactions on polymer surface, lubrication, oxide films, chemi-absorption, catalysis, etc.,

#### Mass spectroscopy

This is a very sensitive method to identify the elemental composition of a film or even any material. It involves the vaporisation in high vacuum of the material, its ionisation, accelerating the different ionised species & analysis them by passing through a strong magnetic field which may also be varying thus separating different species according to their mass to change ratio. These are then collected or recorded on a photographic plate. The basic instrument consists of a sample ionises, an analysis & finally anion collector. The vaporised material is ionised by different methods such as by speak sources, ion bombardment or by laser exciting sources & then alter acceleration allowed to pass through a bent tube under a magnetic field. Ions travelling through the magnetic field will follow different paths whose radio of curvatures will be mass dependent. However, by varying the accelerating voltage it is

### possible to convey ions of different masses successively at the same position of the collector. In the photographic plate the density of ions & their masses are recorded whereas in a collector current are amplified & relative magnitudes recorded. This matro is also known as residual gas analysis method (RGA). This technique has profitably been used for surface film analysis.

According to Ahearn one hundredth of a monolayer of In(113) of 4% abundance in a monolayer of In on a Ge surface has been identified metals like Ag, As, Be, Cr, Cu, Pb& Zn of the order of  $10^{-9}$  atom fractions on contaminated Si Surface have also been detected. Contamination of the level of 50ppm of Ar, Cl, Cr, Cu& Ni in Mo films has also been detected with about  $\pm 25\%$  accuracy. This technique has sensitiveness of about less than nanograms of the element & the material needed is less than 1mg. A micron size of area can be examined with this method.

#### **Nucleation Theories**

In order to explain the nucleation & cluster formation two models namely (a) Capillarity & (b) atomistic or statistical models have been found useful.

#### **Capillarity Model**

This is an extension of the classical theory of volmer – Weber – Becker – Doring for condensation of a supersaturated vapour phase to the liquid state with the formation of spherical droplets in which cluster (or nuclei or embryos) grow by the addition of one atom per reaction with an initial increase in the free energy until a critical size is reached above which the growth can be continued but with a decrease of free energy.

This is then applied to the case of heterogeneous nucleation as for example the cluster formation from a supersaturated vapour phase on a solid substrate other than the vapour phase material. Its basic concept is that during condensation of vapours to solid atoms & eventually to nuclei, there will be an increase of the free energy of formation ( $\Delta G_o$ ) along with the surface energy with the increase of this radii (r) till a critical size (r<sup>\*</sup>) is reached when these will be a decrease in the free energy of formation of a spherical cluster of atoms with the increase of size of nucleus beyond r<sup>\*</sup>. The surface energy coil of course increase with increasing r.

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Gibbs free energy of formation corresponding to the nucleus of critical size  $r^*$  is denoted by  $\Delta G^*$ . These spherical nuclear are, however, unstable and can become stable by an increase of their size. The variations of surface energy, volume energy & total energy of their formation with increasing r at different supersaturation (S=P/Pe). The increase of r is achieved by sequential addition of atoms to the critical nuclear or clusters with consequent

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decrease of free energy of formation (Sum total of surface & volume energy) of the system. It is also seen that higher is the supersaturation the lower will be  $r^* \& \Delta G^* \&$  vice versa. A permanent stable nucleus will be formed when  $r > r^*$ .

Let us consider the free energy of formation in a system containing different phases such as vapour to condensed (V-C). Condensed to substrate (C-S) & Subtrate to vapour (S-V) phases as well as their contact areas,  $\&\Delta G_D$  of an aggregate is related to its size & also its dissociation to vapour phase & is given by

$$\Delta G_0 = a_1 r^2 \sigma_{\nu-c} + a_2 r^2 \sigma_{s-c} - a_2 r^2 \sigma_{s-\nu} + a_3 r^3 \Delta G_{\nu}$$

Where  $a_1r^2$  is the surface area of the aggregate exposed to the vapour phase,  $a_2r^2$  is the contact area between the aggregate & the substrate,  $a_3r_3$  its volume, r being its linear dimension &  $a_1$ ,  $a_2$ ,  $a_3$  being contract.

 $\sigma_{v-c}$  and  $\sigma_{s-c}$  (Positive or negative) are respectively surface & interfacial free energies of the aggregate & $\sigma_{s-v}$  is the surface energy of the substrate expressed in ergS/Cm<sup>2</sup>.  $\Delta G_v$  is the Gibbs free energy of condensation of the film material in the bulk under the same supersaturation condition and it is negative is condensed from molecular volume (V) of the film material is condensed from  $\alpha$  supersaturated vapour pressure P to the equilibrium pressure Pe of bulk liquid then  $\Delta G_v$  is given by

$$\Delta G_{v} = -(\frac{KT}{V}) \ln(P/P_{s})$$
$$= -(\frac{KT}{V}) \ln(R/R_{eb})$$

Where  $R_{e(b)}$  is evaporation rate of monomers (i.e.ad-adoms) from the bulk at the substrate temperature and  $R/R_{e(b)}$  is the supersaturation ratio (S). In the present case  $P_e$  can be taken as the equilibrium pressure of monomers at the substrate temperature.

Now differentiating Eq. 1 a with respect the aggregate size r, we have

$$(\delta\Delta G_0/\delta_r) = 2a_1r\sigma_{\nu-c} + 2a_2r\sigma_{s-c} - 2a_2\sigma_{s-\nu} + 3a_3r^2\Delta G_{\nu}$$

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Assuming there is no change in the shape of aggregate with the increase of r & also no change in  $G_{\nu}, \sigma_{\nu-c}, \sigma_{s-c} \otimes \sigma_{s-\nu}$ 

Now for a critical nucleus i.e.when  $r=r^*$ , the free energy of the total system will be maximum & then  $(S\Delta G_o/S_r) = 0$  under the condition, the size of critical nucleus  $r^*$  can be obtained by rearrangement of EQ.1c. this takes the form

$$r^* = -2 (a_1 \sigma_{v-c} + a_2 \sigma_{s-c} - a_2 \sigma_{s-v})/3a_3 \Delta G_v$$
  
$$\Delta G^* = 4 (a_1 \sigma_{v-c} + a_2 \sigma_{s-c} - a_2 \sigma_{s-v})^3/27a_3^2 \Delta G_v^2$$

Where r is large the contribution of the term containing  $r^3$  in Eq.1a will be predominant than those from the other terms. Since this expression also contains  $\Delta G_V$  which is negative,  $\Delta G_0$  will hence decrease & Ultimately be negative. This is manifestation by the increase of nucleus stability with increasing r beyond r<sup>\*</sup>.

If by some process a few atoms are taken away from a stable cluster so that its size becomes  $r^*$ , then it will dissociate.

Two important factors which, contribute to the dissociation of nuclear are

i) thermal energy and ii) low binding energy.

Hence to obtain a stable film on a substrate, a critical nucleus has initially to be formed & then with the addition of one or more atoms it will become stable.

The enlargement of nuclear takes place from the supply of ad-atoms (monomer's) from the neighbouring areas over the substrate surface with the consequent depletion of adatoms.

Critical sizes of differently shaped nuclear will also be different for a spherical nucleus of a stable liquid phase the free energy of formation  $\Delta G_0$  is related to its surface energy & also to its volume energy of condensation as given by the expression.

$$\Delta G_0 = 4\pi r^2 \sigma_{c-v} + (4/3)\pi r^3 \Delta G_v$$

Corresponding  $\Delta G^* \& r^*$  of the critical nucleus can be obtained by maximising Eq if thus leading to

$$\Delta G^* = (16\pi/3) \left( \sigma_{c-\nu}^3 / \Delta G_{\nu}^2 \right)$$

$$r^* = -2\sigma_{c-\nu}/\Delta G_{\nu}$$
$$= 2\sigma_{c-\nu} V/KT(\ln P/P_e)$$

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It may be mentioned here that in a cluster there will be a numbers of atoms (i) which is related to its radius & volume (v) such that  $i = 4\pi r^3/3V$ . Hence  $\Delta G^*$  r<sup>\*</sup> are replaced by  $\Delta G^*$  r<sup>\*</sup><sub>i</sub> where i indicates the number of atoms, associated with.

In a heterogeneous nucleation say for a cap-shaped embryo on a substrate making a contact angle Q in equilibrium condition, the interfacial free energies are related to Q by the young's expression.

 $\sigma_{s-\nu} = \sigma_{c-s} + \sigma_{c-\nu} \cos \theta$ 

The total free energy of formation can be expressed by

$$\Delta G_0 = \pi r^2 \sin^2 \theta (\sigma_{c-s} - \sigma_{s-v}) + 4\pi r^2 \varphi_1(\theta) \sigma_{c-v} + (4\pi/3) r^3 \varphi_2(\theta) \Delta G_v$$

Where  $\phi_1 \& \phi_2$  are some geometrical functions of Q. Again maximising Eq.i j w.r.t.r, we have the free energy of formation of a nucleus of critical size as given below.

$$\Delta G^* = (16\pi \sigma_{c-\nu}^3 / 3\Delta G_{\nu}^2)\varphi_3(\theta)$$

Where  $\phi_3(\theta) = (2 + \cos\theta) (1 - \cos\theta)^{2/4}$ 

When the equilibrium contact angle  $\theta$  is zero, i.e. when there is complete wetting of the substrate by the condensed phase, then  $\Delta Go^*$  will also be zero & nucleation will be most rapid. If  $\theta$ =180°, i..e.when there is no wetting of the substrate by the condensate  $\phi_3(\theta)$ =1, then equation 1½ reduce to Eq.1g.

The growth of a critical nucleus to supercritical stage and further can take place either by a direct addition of atoms from gaseous phase to the nucleus or by the collision of ad-atom monomers diffusing over the substrate surface. If we consider a relatively small area of the substrate the letter mechanism will be predominant.

In such cases the growth of a critical nucleus will depend on the concentration

The concentration of critical nuclear per unit area  $(N^*)$  is given by the van'thoff isotherm reaction leading to

$$N^* = N_{ad} \exp(-\Delta G^* / KT)$$

Where  $N_{ad}$  is the number of ad-atom monomers at the steady state of equilibrium per unit area.

For a homogeneous case J is given by

$$J = A\omega N^*$$

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A is the surface area of the critical nucleus  $r^* (4\pi r^{*2})$  w is the frequency of impingement  $\{= \propto_c P/(2mKT)^{1/2} \alpha_c$  being the condensation coefficient of vapour atom.

For spherical droplets from the vapour phase Eq.1m takes the form

$$J = Z \propto_c (4\pi r^{*-2}) [P/(2\pi mKT)^{-1/2}] \cdot N_{ad} \exp(-\Delta G^*/KT)$$

Where z is the Zeldovich non-equilibrium factor  $i^*$  is the number of atoms in a critical nucleus & $\sigma$  is the specific interfacial free energy.

For heterogeneous nucleation's of cap-shaped nuclear on a flat solid substrate the rate of nucleation J can be expressed in the form similar to Eq.4m.

$$J = Z\omega, N^*$$

Where w, is the frequency with which a single atom joins the critical nucleus to promote to a stable growth. Since the surface diffusion of ad-atoms is likely to be more predominant then the direct addition .

The frequency w, is given by the product of the probability that an ad=atom adjacent to a critical nucleus (i.e.  $N_{ad} = 2\pi r^* a \sin \theta$ ) & frequency with which an adjacent ad-atom jump to join the nucleus ( $N = \overline{\omega} \exp(-E_D/KT)$ ) where a is the diffusion jump distance. & w is the frequency factor which at Debye temperature becomes nearly equal to Einstein frequency.

 $E_D$  being the activation energy of diffusion.

From the above consideration & also taking into account the statistical correction Eq.10 takes the form.

 $J = C_p \exp[(E_{des} - E_d - \Delta G^*)/KT]$ 

Where C= $(\Delta G^*/4\pi KTi^{*2}2\pi r^*asin\theta.n_0(2\pi mKT)^{1/2})$ 

 $n_o$  is the number of adsorbing sites on the solid substrates lattice.

Nucleation rate J is large for low  $\Delta G^*$  hence for high super saturation i.e for high  $\Delta G_v$ .

#### Atomic (or) Statistical model

In a capillarity model it has been assumed that the bulk thermodynamical properties of a material its surface energetics will also be applicable to nuclei or Clusters which are only of a few atomic dimensions. Walton & Rhodinctal solved this difficulty by introducing partition functions & also taking into consideration the potential energies of different species.

The expression for the rate of nucleation of the critical nuclei with i<sup>\*</sup> atoms is given by the expression.

$$J = Ra^{2}n_{0}(R/\gamma n_{0})^{i*}\exp[\{(i^{*}+1)E_{des} - E_{D} + E_{i}^{*}\}/KT]$$

Where R is the impinging rate, no is the density of in adsorption site on the substrate,

a is the characteristic jump distance of the ad-atoms  $\text{Ei}^*$  is the energy reburied to dissociate the critical nucleus containing i<sup>\*</sup> atoms adsorbed on the surface & $\gamma$  is the ad-atoms monomer vibration frequency (-10<sup>1/2/sec</sup>) for resumption. The rate of nucleation is not directly dependent on  $\sigma$ ,  $\theta$  & G<sub>v</sub>.

The rate of nucleation (J) from critical nuclei containing one, two, three atoms etc. ( $i^* = 1,2,3....$ ) will then be given by the following expressions.

$$J_{i=1}^{*} = Ra^{2}n_{0}\left(\frac{R}{\gamma n_{0}}\right)\exp(2E_{des} - E_{D})/KT$$

$$J_{i=2}^{*} = Ra^{2}n_{0}(R/\gamma n_{0})^{2} \exp\left[\frac{3E_{des} - E_{D} + E_{2}^{*}}{KT}\right]$$

$$J_{i=3}^{*} = Ra^{2}n_{0}(R/\gamma n_{0})^{3} \exp\left[\frac{4E_{des} - E_{D} + E_{3}^{*}}{KT}\right]$$

& so on, for high super saturations the critical cluster may consist of one atom only & at lower supersaturation it may consist of two or more number of atoms.

Let us now consider the formation of a stable  $(1^*+1)$  nucleus from a critical one where  $i^* = 1,2,3$ , etc since the formation of a stable cluster involves some bonds per atom, schematic models for critical nuclei & the corresponding smallest stable cluster are illustrate in Fig.3 for a face centred metal. In the above a, b & c represent the critical nuclei containing 1,2 & 3 a to n respectively & the corresponding smallest stable clusters by d, e & f respectively from a single atom the smallest cluster of two atoms is obtained. The pair of atoms have a single bond per atom. From critical nuclei of 2 & 3 atoms stable clusters of 3 & 4 atoms in triangular & atoms stable clusters of 3 & 4 atoms in triangular & square arrangements respectively are obtained & there correspond to two bonds per atom. The three

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atom stable cluster leads to the {111} orientation of it on D neutral substrate whereas a four atom stable one conforms to a {100} one. From the above consideration a critical of six atoms probably in a hexagonal network arrangement leading to a {0001} orientation on a neutral substrate.

Thus the above Walton – Rhodin theory gives an indication of the development of an oriented plane on a neutral substrate the surface of which does not exact any orientational influence on the impinging atomsto take up any particulars spatial configuration.

The above theory also suggests the appearance of different orientations of the formation of critical nuclei of different atoms depending on the nucleation conditions especially supersaturation & temperature of the substrate etc., These factors favour the formation of alternative nuclei of 3-4, or more atoms at a particular deposition condition. A variation of me orientationmay be caused by a change in the bonding energy of the ad-atoms to the substrate.

Hence the orientation of the initial nucleus is influenced by the bonding as well as by the newly occupied positions which are determined by the substrate temperature.

Fig 1 Walton – Rhodin model for the formation of stable clusters of  $(i^*+1)$  atoms where  $i^*$  is the number of atoms in the critical unstable nucleus; stable clusters d,e& f etc. are corresponding to critical nuclei a,b& c etc., respectively of a face centred cubic metal.

#### FILM GROWTH

There are several stages in the growth process from the initial nucleation of the deposits to the final continuous three dimensional film formation states.

These Stages have been clearly distinguished by pashleyet at as under.

(i) Nucleation (including condensation of vapoues, adsorption of atoms, migration of adatoms, formation of critical nuclei, stable clusters etc., and (ii) growth of layer ones leading to island structure, (iii) coalescence of islands with gaps in between which are interspersed with secondary nuclei. (iv) Joining of layer islands with the formation of channels in between. (v) Finally bridging up the channels with the secondary nuclei to form a continuous film may be with pinholes.

Island Structure Stage (ii)

These islands consist of comparatively layer nuclei or cembalos say greater than 10°A & generally of more dimensional nature with their height, however much less than their lateral dimensions. The formation of these islands & their growth takes place either by direct addition of atoms from the vapour phase or from other environment or by the diffusion controlled process of ad-atoms or both.

The diffusion controlled process is mole commonly observed except at low substrate temperature.

The travel distance of ad-atoms is dependent exponential both on (Edes-Ed) &  $1/\tau$ According to Walton critical nuclei formed from the vapour phase coil consist of about Six or fewer atoms.

A nucleus of about 5°A size is made up of about 20 atoms or so, an island will be made up about 50-100 atoms or mole.

As these islands grow in size these often have tendencies to develop some crystallographic facets during the early stage of their growth & such faceted particles of sizes about 30-50°A could be observed. This feat formation is generally pronounced for oriented nuclei of some metal deposits from vapour phase especially on high vacuum cleaved substrates at high vacuum at higher  $T_s$ . the formation of stable clusters & the subsequent capture of more ad-atoms by diffusion of men to form stable islands.

Coalescence Stage (iii)

There islands as they grow, develop some characteristic shapes & then f with further growth coalesce with the neighbouring ones by rounding off their edges near the joining region (neck). Where these deposits assume a liquid like structure. The coalescence involves considerable transfer of mass between islands by diffusion. Small islands disappear rapidly. The process resembles the sintering of bulk powder where the individual particles assume spherical shapes due to the lowering of their surface energies. During coalescence of two islands which occurs at their necks as well as annealing takes place leading to some definite shapes of layer islands. The time of coalescence is very short say about 0.6 second. This process can take place amongst Islands which are appropriately positioned & the coalesced islands generally become triangles or hexagonal shaped as a result of the rapid decrease of the uncovered substrate surface area followed by a slow rise of it. In the early stages of the

#### Unit – II Electron Diffraction Technique

growth of films it is envisaged that there will be a continuous formation of nuclei & as evaporation progress the nucleation density may increase to about three times the initial ones. After the coalescence of islands to layer masses come nuclei can still be observed in between the large coalesced masses often coalescence by bridging of two particles is pronounced. Channel Stage (iv)

As the coalescence continues with deposition there will be resultant network of the film with channels in between. These channels need not remain void & soon some secondary nuclei start to grow within their void space in the channel with deposition these nuclei will increase in size along with the film thickness in addition to formation of new islands via stage (i) & eventually join the main islands or aggregate secondary islands to the parent body may not be completed or these may not be in perfect matching arrangement with the main aggregate. As a result some of strain may develop due to the stress in between them caused by an insufficient mis-matching of there is the formation of grain boundaries sometimes these channels may not be completely filled up even with increasing film thickness thus leaving some holes or gaps in the aggregate mass ((Fig1.f) with increasing film thickness these holes or gaps will decrease in size.

Continuous film stage (v)

When these gaps are completely bridged by the secondary nuclei film will be continuous however, it often happens that some void space may still remain unbridged. In an ideal continuous film there should not be any gap in the aggregate mass such a stage in a film can be attained only when the film has attained certain average film thickness.

The minimum film thickness for the continuous stage is also dependent on the nature of the deposits modes of deposition parameters etc.,

For a non-metallic deposit such a stage is generally achieved when the average film thickness is say between 500 to 1000°A& for metallic film less. It depends upon the nature of the film material, substrate temperature ( $\tau_s$ ), rate of deposition etc.,

If the deposits do not have sufficient time for recrystallization or annealing before the subsequent unit, multi-coalescence takes place the film will be in a metastable state. The subsequent layer formed over them will also be in such a state.

Thermal annealing treatment (in vacuum) for a sufficient long period of time will cause migration or diffusion of atoms leading to a stable phase. This is known as aging of films.

#### Incorporation of defects impunities etc, in films

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All films are invariably associated with some sort of defects including impurities foreign atoms, grain boundaries, etc.,

Structural defects observed in films can be introduce in any of the stages from (i) to (v) & grain boundaries during the coalescence stage. Air foreign species will tend to concentrate on the grain boundary region of prevent further coalescence or even recrystalization of film deposits. However, the number of grain boundaries can be reduced by the thermal annealing process at an appropriate temperature or using highs  $\tau_s$  while depositing the film.

Defects such as turning, stacking fault, dislocation, miss-matching, etc. can also develop during nucleation's & grain growths. Dislocations in a film can arise due to a slight rotation of two islands with respect to each other or by the presence of grain boundaries in between them. This can also induce a twined structure in a film.

Stacking faults often arise due to the non-thermodynamical equilibrium condition of the deposition. Mis-Matching of atoms at the peripheries of two layer islands or grains may give rise to the antiphase domains. Most of these defects have been observed by numerous workers by electro microscopic studies of films during the growth process.

From these it may generally be said that the initial nuclei are free from defects and but these are incorporated when nuclei tend to be layer & coalescence oculus dislocations are introduced at the boundaries stresses in films may also introduce dislocations stacking faults & twining are also formed during the coalescence stage.

Thickness films often develop surface asperities &roughness& may also be in dendrite, powdery or other forms. Since the growth of a fresh layer may take place not only on the completed but also on a non-completed layer & this often results in the formation of valleys or hills on the growing surface. In such cases impinging atoms from the source will hit the exposed surfaces at different angles especially at the steps, hills or valleys depending on their topography. The amount of material received per unit area per unit time i.e the

## deposition change the incident angles at any point & hence shadowed areas will receive has deposits. Thus a valley which is deeply striking per second per with area than those at the hill top in the direct line of vision with the impinging atoms. All these factors will contribute to the enhancement of the characteristics morphological feature which will be more prominent with increasing film thickness. Hence thickness films generally show dominant morphological features.

A rough surface may also contribute to the morphological features of deposits such a substrate surface will deviate considerably from the mean plane of the surface & it may have micro-valleys hillocks & sides etc. The rate of which impinging atoms hit different areas will differ considerable depending on the solid, angle & the distance from the source etc., This will again result in the enhancement of the surface asperities of the growing deposits. Another factor, which me affect the process is the adsorption of atoms by different areas subtending different solid angles to the vapour source. Since the rate of nucleation also depends upon the adsorption of atoms, the growth may considerably be modified & will differ from area to area leading to an enhancement or decrease orientations observed in a growing film might result from the surface roughness of the substrate.

#### **Deposition Parameters and Grain size**

The grain growth and its size are sensitive to the deposition parameters such as the rate of deposition, substrate temperature along with factors such as diffusion coefficient, mobility of ad-atoms, etc. Some of these factors may enhance or inherit the grain growth and hence the process is quite complex.

The formation of large masses or agglomeration of nuclei increases with the increase of deposition time resulting in the decrease of the nucleation density.

Higher ad-atoms mobility will also increase the agglomeration of films. Some studies have been made on the growth of crystal grains of metallic films with film thickness d-substrate temperature  $T_{s}$ , annealing temperature, and deposition rate. The effect of some of these parameters are schematically shown in Fig.1

The studies of films with increasing thickness both by electron diffraction and microscopy chow the increase of crystallite size of films with the increase of film thickness.

# Electron Diffraction Technique

A higher  $T_s$  generally favors a large grain size due to the increasing mobility of the surface ad-atoms and also increasing cluster formation.

At lower  $T_s$ , the grain size is low since the deposited atoms instead of migrating to the neighbouring grains and increasing their size are condensed and stay stuck to the region to form small nuclei and clusters.

Hence a low  $T_s$  favours a finer size or have amorphous structure as universally observed for all films when deposited at room temperature or below.

The grain size is often too small to yield any coherent electron diffraction termed as amorphous. These are really crystalline in nature having fine grained structures.

Annealing treatments also modify the crystallite sizes and these increase with the increase of annealing temperature.

#### **POSSIBLE QUESTIONS**

#### PART – B

- 1.Explain High energy electron diffraction
- 2.Explain the various stages of film growth
- 3. Write the principle and working of scanning electron microscopy
- 4.Describe the thermodynamics of nucleation
- 5.Explain the X-ray photoelectron spectroscopy
- 6.Explain in detail about the incorporation of defects, impurities, etc. in films
- 7.Write a short note on
- 8.(i) Low energy electron diffraction (ii) High energy electron diffraction
- 9.Explain in detail various stages of film growth
- 10.Describe Low energy electron diffraction
- 11.Briefly explain the nucleation and cluster formation using any one model

#### PART - C

1. Compare and explain low pressure, reactive and R.F. sputtering techniques

#### KARPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE-21

#### DEPARTMENT OF PHYSICS MSC PHYSICS (2017-2019) MATERIAL SCIENCE(17PHP105A) 2017-2018 (ODD) MULTIPLE CHOICE QUESTIONS

#### Unit II

Question	Option 1	Option 2	Option 3	Option 4	Answer
In electron diffraction technique maximum voltage upto	60-63keV	60-65eV	60-65keV	60-63eV	60-65keV
Is used to analyse the surface layers of metals, semiconductor and insulators	SEM	LEED	XPS	HEED	XPS
The surface layers of Ni single crystal was first made by	Davisson	Thomson	germer	both a and b	both a and c
In Finch type camera, a maximum voltage is limited upto	100keV	200keV	65keV	40keV	65keV
In HEED method the accelerating potential of electrons is about	40 to 100keV	60 to 200keV	5 to 500eV	both a and b	both a and b
In LEED method the accelerating potential of electrons is about	5 to 500eV	60 to 200keV	40 to 100keV	none of these	5 to 500eV
For transmission method the material thickness should be lower than	1000Å	500Å	10000Å	13000Å	500Å
The vacuum conditions in LEED is in an order of	10^-9 to 10^-10 torr	10^-4 to 10^-6 torr	10^-1 to 10^-2 torr	< 10^-1 torr	10^-9 to 10^-10 torr
is used as a standard material in HEED	graphite	magnesium	copper	tin	graphite
Which method provide information of both surface layers and different layers constituting the material can be	LEED	HEED	SEM	TEM	HEED
The function of repeller in LEED	cannot passes inelastically scattered electrons	passes inelastically scattered electrons	passes elastically scattered electrons	cannot passes elastically scattered electrons	cannot passes inelastically scattered electrons
A LEED concerns primarily about the nature of the	surface layer	surface contamination	formation of oxide layers	all the above	all the above
Slow electrons because of their low energy interactwith matter	weakly	strongly	mediumly	both a and b	strongly
The resolution in an electron microscope is sbout	5-10Å	<5Å	>5Å	100Å	5-10Å
is one of the most useful and versatile instruments for the investigation of surface topography, microstructural feature, etc.	scanning electron microscope	LEED	HEED	TEM	scanning electron microscope
The secondary electrons have very low energy say	<100eV	>100eV	<50eV	60eV	<50eV

SEM technique along with Is widely used	Auger electron	alaatran miaranraha	field emission	both a and b	both a and b
for surface studies	spectroscopy	election microprobe	microscopy	boun a and b	both a and b
The composition of the surface material is readily	positions of the peaks in	shifts of the ESCA	the shape of the ESCA	all the above	positions of the peaks in
determined from the	the spectra	peaks	peaks	all the above	the spectra
is a very useful tool for the analysis of organic					
compounds and polymer materials of thickness about 40	SEM	LEED	HEED	XPS	XPS
to 100Å					
In SIMS, the sputtered particles come out as	positive ions	negative ions	neutrals	all the above	all the above
The condensation of vapour atoms on a neutral solid takes place from a Condition of vapours	supersaturated	saturated	under saturated	either a or b	supersaturated
nucleation involves film formation over a foreign substrate surface	heterogeneous	homogeneous	either a or b	both a and b	heterogeneous
If the substrate is of the same material as the vapour atoms then the nucleation process is called	homogeneous	heterogeneous	either a or b	both a and b	homogeneous
Formation of critical nucleus involves the of heat of condensation of vapour atoms	release	absorption	adsorption	transfer	release
Impinging atoms can be reflected back to vapour state without	evaporation	condensation	absorption	desorption	condensation
Evaporation can take place at stages	1,2,3 and 4	1,2,3 and 5	1,2 and 3	1,4 and 5	1,2,3 and 5
A higher Ts generally favours a larger grain size due to the increasingof the surface ad-atoms	absorption	adsorption	mobility	condensation	mobility
Asize of area can be examined with mass spectroscopy	micron	nano	cm	mm	micron
If the ions have the same energy, the radii of curvatures will be	mass	volume	density	size	mass
is a very sensitive method to identify the elemental composition of a film	mass spectroscopy	SIMS	SEM	XPS	mass spectroscopy
Adsorbed species after migration collide to form	subcritical nuclei	critical nuclei	cluster	either a or b or c	either a or b or c
In a thermally equilibrated system of impinging atoms, the probability of condensed atoms sticking to the substrate surface is known as	thermal accomodation	sticking coefficient	absorption coefficient	either a or b	either a or b
is a microscopic and short-lived phase(metastable)	surface-solid phase	surface-liquid phase	surface-gas phase	bulk-gas phase	surface-gas phase
Ad-atoms also called	monomers	dimers	trimers	polymers	monomer
When thermal equilibrium is established the flux of					
impinging atoms on the substrate will be equal to theflux of atoms	re-evaporations	desorbed	adsorbed	either a or b	either a or b
The surface diffusion generally takes place by of an ad-atom from one possible site to a next one	jumping	hopping	moving	either a or b	either a or b

The root mean square distance travelled by an ad-atom beforeis an important factor in nucleation process	evaporation	desorption	condensation	none of the above	desorption
In order to explain the nucleation and cluster formation models have been found useful	capillarity	atomistic or statistical models	BCF model	both a and b	both a and b
Capillarity Model is an extension of the classical theory of Volmer-Weber-Becker-Doring forof a supersaturated vapour phase to the liquid state	phase transition	adsorption	condensation	none of the above	condensation
The surface energy will of course increase with	increasing	decreasing	constant	either a or b	increasing
If a molecular volume of the film material is condensed from a supersaturated vapour pressure to equilibrium pressure of bulk liquid $\Delta G_v$ is given by	-(KT/V)ln(p/p <sub>e</sub> )	(KT/V)ln(p/p <sub>e</sub> )	(KT)ln(p/p <sub>e</sub> )	$(KT)\ln(R/R_e)$	-(KT/V)ln(p/pe)
For high supersaturations the critical cluster may consist ofatom	one	two	three	many	one
From critical nuclei of 2 and 3 atoms stable clusters of 3 and 4 atoms in Andarrangements respectively are obtained	single and square	triangular and square	square and hexagonal	triangular and hexagonal	triangular and square
The formation of these islands and their growth take place either by	direct addition of atoms from the vapour phase	from other environment	by the diffusion controlled process of ad- atoms	any of the above	any of the above
Islands consist of comparatively larger nuclei say greater than	10Å	1Å	10nm	1mm	10Å
Thecontrolled process is more commonly observed except at low substrate temperature	evaporation	diffusion	absorption	desorption	diffusion
The smallest stable nuclei are of radii of about	10Å	5Å	10cm	1mm	5Å
Most embryos prior to the formation of island structure are of sizes about	15-30Å	greater than 30Å	less than 15Å	none of the above	15-30Å
An island will be made up aboutatoms or more	50-100	100-200	300-600	10-200	50-100
The surface migration distance of ad-atoms of silver deposited from the vapour phase has been estimated to be about	500nm	500µm	500Å	300nm	500Å
The coalescence involves considerable transfer of Between island by diffusion	atoms	molecules	mass	volume	mass
The time of coalescence is very short say about	0.6second	3second	30second	40second	0.6second
withfilm thickness, holes or gaps will decrease in size	increasing	decreasing	constant	none of the above	increasing

The minimum film thickness for the continuous stage is	nature of the deposits	modes of deposition	deposition parameters	all the above	all the above
The number of can be reduced by the thermal annealing process	foreign species	impurities	grain boundaries	all the above	grain boundaries
Defects such ascan also develop during nucleations and grain growths	twinning	stacking fault	dislocation	all the above	all the above
films often develop surface asperities and roughness	thicker	thin	very thick	none of the above	thicker
The formation of larger masses of nuclei resulting in the Of the nucleation density	decrease	increase	either a or b	no change	decrease
In an electron diffraction camera monochromatic electrons pass through an aperture of a	Diaphragm	Specimen	Focusing coil	Screen	Diaphragm
In electron diffraction camera works as the anode normally at the earth potential	Mono chromatic electron beam source	Specimen	Diaphragm	Focusing coil	Diaphragm
Electron beam should be	Coherent	Monochromatic	High intense	Both a& b	Both a& b

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**Single Crystals:** Significance of single crystals – Crystal growth techniques – The chemical physics of crystal growth – crystal growth phenomena – Nucleation – Gibbs Thomson equation – for vapour – for solution – Spherical nucleus – Heterogeneous nucleation – Cap shaped nucleus – Disc shaped nucleus – Characterisation techniques – XRD spectra and Analysis.

#### Unit – III Single Crystals

#### Significance of single crystals:

The significance of crystal growth to electrical engineering, chemistry and physics is illustrated in fig.1.



Fig.1. Crystal growth as a subject some important connections

The diagram also shows that there are inter dependencies between the individual disciplines and that each of them in turn provides the crystal grower with special assistance. Crystal growth is a vital and fundamendal part of materials science and engineering, since crystals of suitable size.

The volume of silicon single crystals production, the most commonly used domestic electronic material is about  $6 \times 10^4$  metric tons a year, the piezoelectric quartz is  $2.5 \times 10^3$  metric tons a year, the high technology GaAs crystal is about  $1 \times 10^3$  metric tons and the new promising InP crystal is about 10 metric tons.

A decrease of crystal defects and in homogeneities is demanded simultaneously with the development of greater crystal dimensions. The photonic device evolution is due to the advent of compound semiconductor crystal like III-V (GaAs, InP, InSb, GaSb etc.,), II-VI (ZnSe, CdTe,

Zn:CdTe, HgCdTe etc.,) compounds. The major use of GaAs at persent is in the area of microwave devices, high speed digital integrated circuits, and as substrates for epitaxial layer growth to fabricate photonic and electronic devices.

InP is well established as the base material for opto-electronic components in long distance fiber optic communications. Today, parts fabricated from oxide single crystals are used as the active components in laser systems substrates for GaN, Silicon epitaxy, optical components (LiNbO<sub>3</sub>, LiTaO<sub>3</sub>) and substrates for magnetic bubble devices. The emergence of NaI:T1, the scintillation have found wide applications in radiation detective devices.

The halogenide scintallators are among the most wide spread type of scintillation materials and they are classified as two broad groups: Alkali halide scintillators like NaI:T1, CsI: Na, CsI: T1, CsI and fluorperovskites such as liBaF<sub>3</sub>, KMgF<sub>3</sub>, KCaF<sub>3</sub>



Fig.2. Alkali Halide single crystal applications

Inorganic scintillation materials are used for ionizing detectors. The requirements to the scintillators include large photo-absorption fraction, high light yield, fast scintillation decay, fast scintillation rise time and affordable price. Some most attractive oxide scintillation crystals are BGO (Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub>), GSO (Gd<sub>2</sub>SiO<sub>5</sub>: Ce), CdWO<sub>4</sub> and YAP (UAlO<sub>3</sub>:Ce) grown by the Czochralski method. Nonlinear optical (NLO) crystals are very important for laser frequency conversion,

KDP(potassium dihydrogen phosphate) is a suitable crystal for higher harmonic generation of huge laser systems for fusion experiments because it can be grown to larger sizes and also KDP has a high laser damage threshold.

KTP(potassium titany phosphate) is a useful NLO crystal to get efficient green light by the frequency doubling of Nd:YAG laser. It has high optical nonlinearity, large temperature and angular allowance & it is non hygroscopic and mechanically hard. In recent years there has been considerable progress in the development of coherent UV sources based on NLO processes in borate crystals.

The success of their crystals can be attributed to the unique structural characteristics of boron-oxygen groups that confer there compounds with enhanced UV transparency, good nonlinearity and high resistance to laser damage. B- Barium Borate, Lithium Borate, Potassium beryllium boro-fluoride, cesium borate &cesium lithium borate are promising for UV generation because of its wide band gap and adequate optical nonlinearity.

 $CsLiB_6O_{10}$  (CLBO) is more suitable for 4HG (Fourth harmonic generation) and 5HG of Nd:YAG laser. YCa<sub>4</sub>O(BO<sub>2</sub>)<sub>3</sub> (YCOB) and Gd<sub>x</sub>Y<sub>1-x</sub>Ca<sub>4</sub>O(BO<sub>3</sub>)<sub>3</sub> crystals are suitable for second and third harmonic generation of Nd:YAG laser radiation. Organic NLO materials show high optical nonlinearity. L- Arginine phosphate (LAP), 4- dimethylamino-N-methyl-4 stillbazolium tosylate (DAST), urea are some example of organic NLO materials.

Quartz crystals due to the piezoelectric property, ability to rotate a plane of polarization and high transparency in a wide range of wavelengths into UV, Visible and IR regions of the spectrum are widely used in modern electronics and in the field of optical instrumentation. At present the devices determine the research direction and the often-good devices are linked with good "quality" crystals which in turn require good crystal growth equipment.

#### **Crystal growth techniques:**

Growth of crystal ranges from a small inexpensive techniques to a complex sophisticated expensive process and crystallization time ranges from minutes, hours, days and to months.

The basic growth methods are

a) Growth from melt
b) Growth from solution

c) Growth from vapour

The essential task for the crystal growers at present is to gain basic knowledge about the correlation of crystal properties and the growth conditions defined by special parameters.

This basic understanding of the deposition of atoms onto a suitable substrate surfacecrystal growth and the generation of faults in the atomic structure during growth and subsequent cooling to room temperature – crystal defect structure are the input for the design of crystal growth systems and control of growth parameters.

Though the fundamentals are relatively simple, the complexities of the interactions involved and the individuality of different materials, system and growth process have ensured that experimentally verifiable predicates from scientific principles have met with limited success – crystal growth remains an art.

The record advances which include reduction of growth temperatures, the reduction or elimination of reactant transport variables and the use of better controlled energy sources to promote specific reactions, coupled with increased development and application of in-situ diagnostic techniques to monitor and perhaps the ultimate control lead to simplified growth systems.

It is striking that the most important crystal growth techniques which are presently used for semiconductors have been conceived and used by their inventors. M.Sc PHYSICS 2017-2018 (ODD)

Unit – III Single Crystals

Growth method	Inventor	Year	Original Aim
Czochralski	Czochralski	1917	Investigation on the rate of
			crystallization of metals.
Bridgman	Obereimov	1924	Growth of metal crystals (Bi, Sn
	Schubnikov		, Zn , Mg , Al , Cu)
	Bridgman	1925	Growth of metal crystals (W, Sb, Bi, Te, Zn, Sn)
	Staber	1925	Growth of NaNo₃ , Bi , Zn crystals
	Stockbarger	1936	Growth of alkali halide crystals (KBr, LiF)
Zone melting in	Kapitza	1928	Purification and crystal growth of
crucible			Bi
	Pfann	1952	Purification of Ge
Floating zone	Keck, Golay Emei	1953	Purification of Si
	S	1954	Purification of Si
Nacken Kyropoulos	Nacken	1916	Growth of salol and
			benzophenone crystals
	Kyropoulos	1926	Growth of alkali halide crystals

#### The Chemical Physics of crystal Growth:

If the crystal is in dynamic equilibrium with its parent phase the free energy is at a minimum and no growth will occur. For growth to occur this equilibrium must be distributed by a change of the correct sign in temperature, in pressure, chemical potential (eg: saturation) electrochemical potential (eg: electrolysis) or sbrain(solid state growth)

The system may then release energy to its surrounding to compensate for the decrease in entropy occasioned by the ordering of atoms in the crystal and the evolution of heat of crystalisation. In a well designed growth process just one of these parameters is held minimally away from its equilibrium value to provide a driving force for growth.

Crystal growth then is a non – equilibrium process and though must be given to the temperature and concentration and other gradients and the fact that heat of crystalisation is evolved and must be kept as near equilibrium and as near to a steady state process as possible. That is why control of the crystal growth environment and a consideration of growth kinetics both at the macroscopic and the atomic levels are of vital importance to the success of a crystal growth experiment.

In some growth techniques there is no crystal initially present. Here the nucleation problem is met which in essence is due to the fact that the surface to volume ratio of small particle is much higher than for a large crystal. Surfaces cost energy because of discontinuous in atomic bonding. This nucleation of a new phase is discontinuous not a quasi equilibrium process. This is the reason why pure melts super cool and solutions become supersaturated. Thus the growth system departs considerably from equilibrium before a crystal nucleates and when it comes the new born crystal grows very rapidly at first and is full of defects , some of which propagate on into the later stages of near equilibrium growth. Crystal growers thus seek to use methods where a seed crystal can be introduced into the system to avoid the nucleation.

In the last three decades great strides have been made toward achieving crystal perfection motivated by the needs of the electronics and optics industries. While thermodynamics excludes the possibility of growing a perfect crystal, gross defects like grain

boundaries, voids and even dislocations can be eliminated with case and point defects like impurities, vacancies, interstitials and anti structure disorder can be minimized by attention to growth environment and purity of reagents and apparatus.

# **CRYSTAL GROWTH PHENOMENA**

## Introduction:-

The growth of crystals from liquid and gaseous solutions pure liquids and pure gases can only occur if some degree of super saturation or supercooling has first been achieved in the system. The attainment of the supersaturated state is essential for any crystallization operation and the degree of supersaturation or deviation from the equilibrium saturated condition is the prime factor controlling the deposition process.

Growth of crystals can be considered to comprise three basic steps:

- Achievement of supersaturation or supercooling
- Formation of crystal nuclei of microscopic size
- Successive growth of crystals to yield distinct faces.

## Nucleation:-

Nucleation is an important phenomenon in crystal growth and is the precursor of crystal growth and of the overall crystallization process. Before crystals can grow there must exist in the solution a number of minute solid bodies known as centers of crystallization, seeds, embryos or nuclei.

In a supersaturated or supercooled system when few atoms or molecules join together a change in free energy takes place in the process of formation of a cluster in a new phase. The cluster consisting of such atoms or molecules is called nuclei.

The kinetics of phase change take place in four different stages viz.,

- The development of the supersaturated state which may arise due to chemical or photochemical reaction or the consequence of a change in temperature , pressure , tension or other chemical or physical condition.
- The generation of minute specks or nuclei

- The growth of nuclei to form particles of macroscopic dimensions or domains of the new phase
- The relaxation processes such as agglomeration by which the texture of the new phases changes.

Nucleation may occur spontaneously or it may be induced artificially. Based on these nucleation is classified as two kinds viz.,

- Homogeneous nucleation
- Heterogeneous nucleation

The spontaneous formation of crystalline nuclei in the interior of the parent phase is called homogeneous nucleation. On the other hand if the nuclei form heterogeneously around ions, impurity molecules or on dust particles on surfaces or at structural singularities such as dislocations or other imperfections, it is called heterogenous nucleation.

The nucleation process was understood after realising the undercooled and supersaturated phases, which refers the unstable conditions. When the pressure of the vapour P is less than, equal to , or greater than the vapour pressure of the liquid phase at the same temperature known as equilibrium pressure  $P^*$ , the vapour is described as undersaturated , saturated , or supersaturated with respect to the liquid phase.

The undersaturated state and saturated state are thermodynamically stable. But the supersaturated state is unstable; i.e., a supersaturated vapour in contact with the bulk liquid phase will condense on to the liquid until saturation is obtained. In a supersaturated vapour, not only single molecules A, are present but also embryos which are clusters of molecules bound together by their intermolecular interactions.

The mechanism of formation of such embryos is the simple collision process consisting of a single molecule A, with a cluster Ai-1 consisting of (i-1) molecules and thus giving rise to a cluster Ai; i.e.,

 $A_1 + Ai - 1 \rightarrow Ai \rightarrow 1$ 

Unit – III Single Crystals

The cluster Ai may also be formed by the evaporation of a molecule from some cluster Ai+1 ; i.e,

 $Ai+1 \rightarrow Ai+A_{\text{1}}$ 

The phase change takes place by single molecules becoming attatched to embryos of various sizes; these processes predominate slightly over the reserve process in which the various embryos lose single molecules.

The size distribution of embryos changes with time, the number of the larger ones increasing. There is a critical size which is in unstable equilibrium with the supersaturated; this is a critical nucleus the formation of which constitutes the bottleneck of the phase change. Once embryos achieve the critical size there is a high probability that they will grow, relatively unhindered, the microscopic size.

# **THEORIES OF NUCLEATION:-**

Gibbs was the first to realize that the formation of small embryonic clusters with some critical size is a prerequisite for a microscopic phase transformation to take place. Owing to their increased surface – volume ratio such clusters termed critical nuclei. Have more energy than bulk phase of the same moss. Hence, they have a chance to survive and to produce microscopic entities of the new phase only within supersaturated or undercooled systems.

As a matter of fat, the equilibrium between the critical nucleus and its environment is unstable provided that the volume of the whole system is not very small. Nucleation is very rare example of a process whose activation energy can be calculated solely on the basis of phenomenological thermodynamics.

## **Theories of nucleation:**

Gibbs was the first to realise that the formation of small embryonic clusters with some critical size is a prerequisite for a microscopic phase transformation to take place. Owing to their increased surface – volume ratio such clusters, termed critical nuclei, have more energy than bulk phases of the same mass. Hence they have a change to survive and to produce microscopic entities of the new phase only within supersaturated or undercooled system.

As a matter of fact, the equilibrium between the critical nucleus and its environment is unstable. Provided that the volume of the whole system is not very small

#### Gibbs Thomson equation for vapour:

In 1806, laplace obtained the condition for the mechanical equilibrium of a surface. For a spherical liquid the pressure  $P_{11r}$  within the drop

$$P_{11r} - P_1 = \frac{2\sigma}{r}$$
 ------ (1)

Where is the radius of the drop,  $\sigma$  is the surface tension and P<sub>1</sub> is the pressure in the parent phase outside the drop

In 1870, William Thomson showed that the vapour pressure  $P_1$  of a liquid in the form of drop of radius r is greater than  $P_{1\infty}$ , the saturation vapour pressure over plane liquid surface (r =  $\infty$ ). Let the chemical potentials of the saturated vaour and the liquid with a plane interface be  $\mu_{1\infty}$  and  $\mu_{11\infty}$ 

For equilibrium condition

 $\mu_{1\infty} = \mu_{11\infty}$  ------ (2)

Similarly, let  $\mu_r$  be the chemical potential of the vapour in equilibrium with the small liquid droplet of radius r and chemical potential  $\mu_{11r}$ . then

$$\mu_{1r} = \mu_{11r}$$
 ------ (3)

If  $P_{11}$  is the pressure within the liquid, the chemical potential of the liquid phase  $\mu_{11}$  varies with  $P_{11}$  as

$$\left[\frac{\partial \mu_{11}}{\partial P_{11}}\right]_{\mathrm{T}} = \mathbf{V}_{11} \tag{4}$$

Where  $V_{11}$  is the volume per molecule in the liquid drop the pressure within the liquid with a plane surface is  $P_{1\infty}$  and within the droplet it is

$$P_1 + \frac{2\sigma}{r} \tag{5}$$

Integrating eqn (4) between these limits and since  $P_1 - P_{1\infty}$  is very small compared to  $2\sigma/r$  we can write,

$$\mu_{11r} - \mu_{11\infty} = \frac{2\sigma}{r} V_{11}$$
 (6)

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From equation (2)

$$\mu_{1r} - \mu_{1\infty} = \frac{2\sigma}{r} V_{11}$$
 ------(7)

The chemical potential in term s of pressure is

$$\mu_1 = \mu_1 + KT \ln P_1$$
 ------ (8)

Where,  $\mu_1$  is the chemical potential of the vapour when  $P_1 = \infty$ . Substituting for  $\mu_{1r}$  and  $\mu_{1\infty}$  in equation (7) we obtain

$$KTln \frac{P_1}{P_{1\infty}} = \frac{2\sigma V_{11}}{r}$$
(9)

The relation represented in eqn. (9) is known a Gibbs- Thomson equation.

#### **Gibbs – Thomson equation for solution:**

Gibbs – Thomson equation can also be applied when a crystal (second phase) is formed in a supersaturated solution (first phase). The solubility of a crystal increases as the size of the crystal decreases. If  $C_1$  and  $C_{\infty}$  are the concentrations of solution with a small crystal of radius r and with a large crystal of radius  $r = \infty$  respectively then

$$\mathrm{KTln}\frac{C_1}{C_{1\infty}} = \frac{2\sigma V_{11}}{r}$$
(10)

A supersaturated solution with a supersaturated ratio of  $C_1/C_{1\infty}$  can be equilibrium with a crystal if the size r satisfies eqn. (10). Any crystal larger than r will grow in this supersaturated solution since its solubility is smaller than  $C_1$  and crystal smaller than r will dissolve in this supersaturated solution since its solubility is greater than  $C_1$ .

#### **Spherical nucleus**

The crystal nucleus will not have a regular morphology of a crystal since it normally contains of atoms or molecules. Under such condition, the critical nucleus can be assigned spherical shape. When a droplet nucleus forms due to supersaturation of vapour, certain quantity of energy is spent in the creation of a new phase. The free energy change associated with the formation of a nucleus can be written as

$$\Delta G = \Delta G_s + \Delta G_v \tag{11}$$

Where,  $\Delta G_s$  is the surface excess free energy and  $\Delta G_v$  is the volume excess free energy. For the spherical nucleus

Where,  $\Delta G$  is the free energy change per unit volume which is a negative quantity. Since the surface energy term increases with  $r^2$  and the volume energy term decreases with  $r^3$ , the net free energy change increases with the increase in size, attains the maximum and decreases for further increase in the size of the nucleus (Fig.1). The size corresponding to the maximum free energy change is called critical nucleus. The radius of the critical nucleus is obtained by setting the condition.

$$\frac{d\Delta G}{dr} = 0 \tag{13}$$

and the expression for critical radius is given by

$$\mathbf{r}^* = \frac{-2\sigma}{\Delta G_{\mathbf{v}}} \tag{14}$$

Substituting the volume of  $r^*$  in eqn. (2) the free energy change associated with the critical nucleus is obtained as

This can be shown to be equal to one third of the surface energy of the critical nucleus. The expressions for  $\Delta G_s$  are given for the nucleation from vapour, solution and melt using Gibbs-Thomson equation as follows

$$\Delta G_{\rm r} = \frac{-KT}{v} \ln \frac{P}{P^*} = \frac{-KT}{v} \ln S \quad (\text{vapour}) \tag{16}$$

$$\Delta G_{v} = \frac{-KT}{v} \ln \frac{C}{C^{*}} = \frac{-KT}{v} \ln S \quad \text{(Solution)}$$
 (17)

Where, K is the Boltzman constant, S is the supersaturation,  $\Delta T$  is the supercooling,  $T_m$  is the melting point and  $\Delta H_m$  is the heat of fusion. The number of critical nuclei formed per unit time per unit volume is known as the rate of nucleation.

#### **Heterogeneous nucleation:**

The nucleation rate will be affected considerably due to the presence of impurities. Turnball proposed that the energy of formation of a critical nucleus can be catalyzed by a suitable surface in contact with the nucleus. The nucleation catalyst or nucleant may be a solid particle suspended in the liquid, the surface of the container or a solid surface. This process of nucleation on the surface of a nucleant is known as heterogeneous nucleation.

In heterogeneous nucleation, the reaction may be the direct exchange of monomers between the parent phase and the cmbryo or through the surface which is normally known as substrate.

The heterogeneous nucleation rate is given in a more general way as

$$J(i^*) = Z\beta^*C(i^*)$$
 ------(19)

Where, Z is the zeldovich factor or the non-equilibrium constant.  $\beta^*$  is the impingement term and C(i<sup>\*</sup>) is the concentration of the critical nuclei. The concentration of the critical nuclei is given as

 $C(i^*) = C(1)exp[-\Delta G(i^*)/KT]$ 

----- (20)

Where,  $\Delta G(i^*)$  is the free energy of formation of a critical nucleus under heterogeneous condition. The properties of the clusters are considered to be same as those in the bulk to mathematical simplicity, using the above capillarity approximation the nucleation parameters for various shapes of embryo are evaluated for heterogeneous nucleation.

#### **Cap** – shaped nucleus:



Fig.1. Cap-shaped embryo wetting the substrate with a contact angle  $\theta$ 

Fig.1. represents the cap shaped embryo wetting the substrate with a contact angle  $\theta$ . The free energy change for the formation of the embryo, taking into account the not inter facial free energy and the volume free energy change is

Where,

$$\Delta G_{\rm v} = \frac{-{\rm KT}}{{\rm v}} \ln \frac{{\rm P}}{{\rm P}^*} \tag{22}$$

 $\sigma_{sx}$ ,  $\sigma_{sv}$  and  $\sigma_{vx}$  are the interfacial energies between liquid-substrate, vapour-substrate and vapour-liquid respectively. Using the young equation for the equilibrium condition.

$$\sigma_{sv} = \sigma_{sx} + \sigma_{vx} \cos\theta \qquad ------(23)$$

using eqn. (1) the eqn. (3) is written as

Maximizing eqn. (4) the critical parameters of the embryo are

$$\mathbf{r}^* = -\frac{-2\sigma_{\mathbf{v}\mathbf{x}}}{\Delta G_{\mathbf{v}}} \tag{25}$$

and

$$\Delta G^* = \frac{16}{3} \frac{\pi \sigma_{Vx}^3}{\Delta G_V^2} \,\phi(\theta) \tag{26}$$

----- (28)

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Where,  $\varphi(\theta) = \frac{2 - 3\cos\theta + \cos^3\theta}{4}$  ------(27)

Which varies between 0(for  $\theta$ =0) and 1(for  $\theta$ =180)

$$(\Delta G^*)_{hot} = (\Delta G^*)_{hom} \phi(\theta)$$

The critical free energy change of the nucleus in the case of heterogeneous nucleation in thus lowered for all sizes by the multiplication factor  $\varphi(\theta)$  because of the embryo-substrate interaction. The curvature of the critical embryo is not affected and the Gibbs- Thomson equation is still valid.

#### **Disc- shaped nucleus:**

The other possible shape to be considered is disc- shaped embryo with radius r and height h. Let  $\sigma_{vx}$ ,  $\sigma_{sx}$  and  $\sigma_{sv}$  be the interfacial energies between vapour-liquid, liquid-substrate and vapour-substrate and  $\sigma_e$  the interfacial energy of the curved surface. The free energy of formation is

Maximizing the eqn. (1) with respect to h and r, the critical parameters of the nucleus are

and

$$\Delta G^* = \frac{4\pi\sigma_e^2}{\Delta G_v^2} (\sigma_{vx} + \sigma_{sx} - \sigma_{sv})$$
(32)

#### Heterogeneous nucleation derivation:



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 $G_s = \gamma_{vx}.A_{vx} + \gamma_{sx}.A_{sx} + \gamma_{vs}.A_{vs}$ 

Where, Avx, Avs and Asx are areas of vx, sx and vs interfaces respectively

Assume  $\gamma$  be the radius of the droplet, then

$$A_{xs} = \pi r^2 \sin^2 \theta$$
  

$$A_{vs} = A_o - \pi r^2 \sin^2 \theta; A_o \text{ is the area of xs interface without x}$$
  

$$A_{vx} = \int_0^{\theta} (2\pi r \sin \epsilon) (r d\epsilon) = 2\pi r^2 (1 - \cos \theta)$$

Thus, we have

$$dr = \frac{r\sin\theta(1+\cos\theta)}{(2-\cos\theta-\cos^2\theta)}d\theta$$

$$\cos\theta = \frac{\gamma_{vs-\gamma_{xs}}}{\gamma_{vx}}$$

$$\Delta G(r) = V_x \Delta G_v + \gamma_{vx} A_{vx} + (\gamma_{xs} - \gamma_{vs})A_{xv}$$

$$= \frac{\pi r^3}{3}(2 - 3\cos\theta + \cos^3_{\theta})\Delta Gv + \gamma_{vx}2\pi r^2(1 - \cos\theta) + (\gamma_{xs} - \gamma_{vs})\pi r^2 \sin^2_{\theta}\theta$$

$$\gamma_{xs} - \gamma_{vs} = -\gamma_{vx}\cos\theta$$

Replacing this into above equation then we have

$$\Delta G(\mathbf{r}) = \left[\frac{4\pi}{3}\mathbf{r}^{3}\Delta G\mathbf{v} + 4\pi\mathbf{r}^{2}\gamma_{vx}\right] \cdot \left[\frac{2-3\cos\theta+\cos^{3}_{\theta}}{4}\right]$$

 $\theta = 180^{\circ} \rightarrow$  no wetting of the surface and thus no catalyst by the surface

 $\theta = 0 \rightarrow$  full wetting fully catalyzed, no barrier for nucleation at surface

#### **XRD** (X-Ray Diffraction):

X- Ray's are electromagnetic radiation of wavelength about  $1\text{\AA}(10^{-10} \text{ m})$ , which is about the same size as an atom. The discovery of X-Ray in 1895 enabled scientist to probe crystalline structure at the atom level. XRD has been in use in two main areas, for the finger print characterization of crystalline materials and the determination of their structure.

## **Production of X-Rays:**





X-Rays are produced by bombarding a metal target (Cu, Mo usually) with a beam of electrons emitted from a hot filament (often tungsten). The incident beam will ionize electrons from the target atom and X-Rays are emitted a the resultant vacancies are filled by electrons dropping down from L(2p) or M (3p) levels, this gives rise to  $k_a$  and  $k_b$  lines.

## **X-Ray Generation:**



As the atomic number Z of the target element increases, the energy of the characteristic emission increases and the wavelength decreases.

Moseley's law  $(C/1)^{1/2} \propto Z$ 

## **Principles of X-Ray Diffraction:**

- X-Rays are passed through a crystalline material and the patterns give information of size and shape of the unit cell
- X-Rays passing through a crystal will be bent at various angles: this process is called diffraction
- X-Rays interact with electrons in matter, i.e., are scattered by the electron clouds of atoms
- The angles at which X-Rays are diffracted depends on the distance between adjacent layer of atoms or ions. X-Rays that hit adjacent layers can add their energies constructively when they are "in phase". This produces dark dots on a detector plate.



Unit – III Single Crystals

## **Bragg's law and Diffraction:**

 $n\lambda = 2dsin\theta$ . Where, n is the integer

Diffraction occurs only when Bragg's law is satisfied condition for constructive interference (X-Rays 1&2) from planes with spacing d.



#### The powder techniques:

An X-Ray beam diffracted from a lattice plane can be detected when the X-Ray source, the sample and the detectors are correctly oriented to give Bragg's diffraction



- ✤ All orientations present
- Continuous "debye" rings
- Linear diffraction pattern with discrete "reflections" obtained by scanning through are that intersects each debye cone at a single point
- Each cone consists of a set of closely space dots each one of hich represents a diffraction from a single crystallite

## What information De we get from powder XRD:

- Lattice parameters
- Phase intensity
- Phase purity
- **•** Crystallinity
- Crystal structure
- Percent phase composition

#### **Data collection:**

- The scattering intensity drops as  $\frac{1}{2}(1+\cos^2 2\theta)$
- A good range is  $10-70^{\circ}$  at  $2\theta$
- Routine analysis may only take 30-60 min
- ♣ Data for rietveld analysis may take 12-18 hrs to collect

#### Data analysis:

- To confirm a known material, search using the JCPDS (Joint Committee on Powder Diffraction Standards) data base. They have about 100,000 patterns on file
- ➢ For a new material, need to index the pattern

Unit – III Single Crystals

## Single crystal techniques:



#### **Application of single crystal XRD:**

- Used for precise determination of a unit cell, including cell dimensions and positions of atoms with the lattice. Bond lengths and angles are directly releted to the atomic positions
- Characterization of cation-anion coordination
- Variation in crystal lattice with chemistry
- With specialized chambers, structures of high pressure and or temperature phases can be determined
- Powder patterns can also be derived from single- crystal by use of specialized cameras

#### Limitations:

- ✤ Optically clear sample
- ✤ Twinned samples can be handled with difficulty
- ✤ Data collection generally requires between 24 and 72 hours

## Unit – III Single Crystals

#### **POSSIBLE QUESTIONS**

## PART - B

- 1. Derive the Gibbs Thomson equation for vapor and solution
- 2.Explain the spherical nucleus
- 3.Explain significance of single crystals
- 4. What is meant by Nucleation? Explain its importance in crystal growth
- 5.Write a note on crystal growth techniques
- 6.Explain the principle of XRD and how XRD spectra was analyzed
- 7.Derive the Gibbs Thomson equation for vapor and solution
- 8.Briefly explain the cap shaped nucleus and disc shaped nucleus
- 9.Derive the Gibbs Thomson equation for vapor and solution
- 10.Explain the spherical nucleus

## PART- C

1.Explain principle and working of scanning electron microscopy and mass spectroscopy with suitable diagram

#### KARPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE-21

#### DEPARTMENT OF PHYSICS MSC PHYSICS (2017-2019) MATERIAL SCIENCE(17PHP105A) 2017-2018 (ODD) MULTIPLE CHOICE QUESTIONS

#### Unit III

Question	Option 1	Option 2	Option 3	Option 4	Answer
In the crystal growth process, supersaturation will be	when temperature	when temperature	when salt dissolves	none of these	when temperature
attained	increases	decreases	completely	none of these	increases
Heterogeneous nucleation is typically much faster than					
homogeneous nucleation because nucleation barrier is	higher	much lower	much higher	lower	much lower
at a surface					
The solubility diagram is between temperature and	concentration	time	pressure	none of these	concentration
Bridgman crystal growth method is based on	gel growth	solution growth	melt growth	vapour growth	melt growth
The spontaneous formation of crystalline nuclei in the	Homogeneous nucleation	hataraganaous nucleation	instability	seed	Homogeneous nucleation
interior of the parent phase is called	fiomogeneous nucleation	neterogeneous nucleation	liistaoliity	seeu	Tomogeneous nucleation
A crucible used in the bridgman crystal growth method	auartz	مامده	plactics	metals	mertz
is	quartz	giass	plastics	lifetais	qualiz
The gibbs free energy changes from	0 to infinity	-1 to 0	0 to 1	none of these	0 to infinity
The solubility of most substances With	does not relate	increases	decreases	none of these	increases
temperature		mereuses	accicases	none of these	mereuses
According to BCF theory, the important factor for growth	surface diffusion	volume diffusion	ternary growth	pressure	surface diffusion
parameter is	Surface annusion	volume unrusion	ternary growth	pressure	surface annusion
The vapour transport is carried out in	crucibles	Al rod	quartz	silicon	Al rod
An example for physical gel is	silica	polyacrylamide	tetramethoxy silane	agar-agar	silica
A decrease of crystalis demanded					
simultaneously with the development of greater crystal	defects	quality	inhomogeneities	both a and c	both a and c
dimensions					
The photonic device evolution is due to the advent of	compound semiconductor	metal-organic	organic	inorganic	compound semiconductor
Crystals	compound semiconductor	inetar organie	organie	morganie	compound semiconductor
The major use of $GaAs$ at present is in the area of	microwave devices	high speed digital	substrates for epitaxial layer growth	all the above	all the above
The major use of Garts at present is in the area of		integrated circuits			
InP is well established as the base material for	optical components	electronic component	mechanical component	opto-electronic	opto-electronic
	optical components	electronic component	meenamear component	components	components
The are among the most widespread type	ovide crystals	organic crystals	halogenide scintillators	quartz	halogenide scintillators
of scintillation materials	oxide el ystais	organic erystais	naiogenide semimators	quartz	naiogenide semunators
Alkali halide scintillators like	NaI:TI	KMgF3	CsCaBr3	RbMgF3	NaI:TI
Fluorperovskites such as	CsSrBr3	LiF:Eu	CsI	LiF:Eu	CsSrBr3
The applications of alkali halide scintillators are	UV applications	ultrasound applications	IR optics	all the above	all the above
Pick one of the requirements for the scintillators	slow scintillation decay	fast scintillation rise	low light yield	slow scintillation rise	fast scintillation rise
Attractive oxide scintillation crystals are	BGO	KCaF3	NaI:TI	KDP	BGO

Nonlinear optical crystals are very important for	Jewelry	watch	scintillation	laser frequency conversion	laser frequency conversion
KDP is a suitable crystal for Of huge laser systems for fusion experiments	high harmonic generation	low harmonic generation	Acousto optic crystals	semiconductors	high harmonic generation
KTP is	hygroscopic	non hygroscopic	mechanically hard	both b and c	both b and c
Borate crystals are used in	IR optics	NLO	coherent UV sources	all the above	coherent UV sources
The success of the borate crystals can be attributed to the unique structural characteristics of Groups	boron-oxygen	boron	oxygen	halide	boron-oxygen
Pick one of the following which is promising for UV generation	beta-barium borate	LiF:Eu	KDP	КТР	beta-barium borate
is more suitable for 4HG and 5HG of Nd:YAG laser	yittrium calcium borate	cesium lithium borate	KDP	КТР	cesium lithium borate
are suitable for 2nd and 3rd harmonic generation of Nd:YAG laser radiation	YCa4O(BO3)3	GdxY1-xCa4O(BO3)3	cesium lithium borate	both a and b	both a and b
Choose organic NLO materials from the following	L-Arginine phophate	urea	4-dimethylamino-N- methyl-4-stilbazolium tosylate	all the above	all the above
crystals due to the piezoelectric property and ability to rotate a plane of polarization and high transparency are used in electronics and optical instrumentation	Quartz	KDP	urea	all the above	Quartz
KTP is a useful nonlinear optical crystal to get efficient green light by the frequency doubling of	Nd:YAG laser	He-Ne laser	Ti:Sapphire laser	all the above	Nd:YAG
Crystal growth is aprocess	non-equilibrium	equilibrium	stable	none of these	non-equilibrium
Many Properties of Are obscured by the effects of grain boundaries	physical and liquids	magnetic and solid	physical and solids	physical and gas	physical and solids
Growth methods are classified intotypes	three	two	four	none of these	three
The third step in the growth of crystals is	successive growth of crystals to yield distinct faces	achievement of supersaturation	formation of crystal nuclei	supercooling	successive growth of crystals to yield distinct faces
The cluster consisting of few atoms or molecules is called	nuclei	seed	crystal	polycrystal	nuclei
The kinetics of phase change take place in Different stages	five	three	four	two	four
The development of the supersaturated state may arise due to change in	temperature	pressure	chemical or physical condition	all the above	all the above
Once embryos achieve the Size there is a high probability that they will grow	nano	micro	bulk	critical	critical
critical nuclei have more than bulk phases of the same mass	pressure	concentration	energy	energy and concentration	energy
William Thomson showed that the vapour pressure of a liquid in the form of a drop of radius r is greater than	vapour pressure over a plane liquid surface	saturation vapour pressure over a plane liquid surface	vapour pressure inside a liquid	none of these	saturation vapour pressure over a plane liquid surface

J.J.Thomson modified Thomsons equation to show that the melting point of a small crystal isof a crystal	less than that	more than that	equal	a or b	less than that
Since the two phases(i.e. crystal and supercooled melt) are in equilibrium, their chemical potentials must be	equal	not equal	high	low	equal
The solubility of a crystal increases as the size of the crystal	decreases	increases	not changes	a or b	decreases
If $C_1$ and $C_\infty$ are the concentrations of solution with a small crystal of radius r and with a large crystal of radius $r = \infty$ respectively then	$KTln(C_1/Ci_{\infty})=2\sigma V_{II}/r$	KTln(CI∞/C1)=2σV <sub>II</sub> /r	$KTln(C_1/CI_{\infty})=2\sigma V_{II}$	$KTln(C_1/CI_{\infty})=\sigma V_{II}$	$KTln(C_1/Ci_{\infty})=2\sigma V_{II}/r$
Any crystal smaller than r will dissolve in the supersaturated solution since its solubility is $\dots$ than C <sub>1</sub>	lower	greater	equal	a or b	greater
The size corresponding to the maximum free change is called	nucleus	small nucleus	critical nucleus	large nucleus	critical nucleus
The surface energy term with $r^2$ and the volume energy term With $r^3$	decreases, increases	increases, decreases	constant, increases	decreases,constant	increases,decreases
The free energy change associated with the critical nucleus is	$\Delta G^{*}=16\pi\sigma^{3}/3\Delta {G_{v}}^{2}$	$\Delta G^{*}=16\pi\sigma^{2}/3\Delta {G_{v}}^{2}$	$\Delta G^* = \pi \sigma^3 / 3 \Delta G_v^2$	$\Delta G^{*}=16\pi\sigma^{3}/\Delta {G_{v}}^{2}$	$\Delta G^{*}=16\pi\sigma^{3}/3\Delta {G_{v}}^{2}$
The expression for $\Delta G_v$ for the nucleation from solution is given by	$\Delta G_v = -(kT/v) \ln S$	$\Delta G_v = (kT/v) \ln S$	$\Delta G_v = -(kT) lnS$	$\Delta G_v = -\ln S$	$\Delta G_v = -(kT/v) lnS$
The number of critical nuclei formed per unit time per unit volume is known as the	rate of formation	nucleation	rate of nucleation	seed growth	rate of nucleation
The nucleation on the surface of a nucleant is known as	heterogeneous nucleation	homogeneous nucleation	homo or heterogeneous nucleation	none of these	heterogeneous nucleation
The concentration of the critical nuclei is given as	$C(i^*)=C(1)exp[-\Delta G(i^*)]$	$C(i)=C(1)\exp[\Delta G(i^*)/kT]$	$C(i^*)=exp[\Delta G(i^*)/kT]$	$C(i^*)=C(1)exp[-\Delta G(i^*)/kT]$	$C(i^*)=C(1)exp[-\Delta G(i^*)/kT]$
$\sigma_{sv}$ is the interfacial energies between	liquid-substrate	vapour-substrate	vapour-solid	substrate-vapour	vapour-substrate
The frequency of the continuous X-rays emitted from the tube	do not depend on the target	depends only on the potential difference	directly proportional to the potential difference	all of the above	all of the above
The frequencies of the characteristic X-rays emitted from an X-ray tube	do not depend on potential difference	depends only on the atomic number of the target	can be increased by increasing atomic number of target	all of the above	all of the above
The penetrating power of X-rays emitted from an X-ray tube depends on	filament current	applied potential difference	atomic number of target	both b and c	both b and c
which of the following can be deflected by an electric field	X-rays	UV-rays	cathode rays	microwaves	cathode rays
The order of the wavelength of X-rays is	$10^{-10}$ m	1m	10 <sup>-6</sup> m	10 <sup>-4</sup> Å	$10^{-10}$ m

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# SYLLABUS

**Singular and rough faces:** Models on surface roughness – The Kossel, Stranski, Volmer (KSV) theory – The Burton, Cabrera and Frank (BCF) theory – BCF theory of solution growth – Periodic Bond chain theory – the Muller – Krumbhaar Model.

The Bridgman and related techniques – Crystal pulling techniques – Convection in melts – Modeling and simulation of bulk crystal growth considering melt dynamics – Melt growth of oxide crystals for saw, piezo electric and non linear optical applications – Liquid encapsulated and Czochralski technique – Zone melting technique – Skull melting process – Heat exchanger method.

#### Models on surface roughness

Several calculations have been performed of the degree of roughness of a crystal surface and its variations with temperature.

Buston and Cabrera (1949) used the Onsager (1944) solution of the Sing model to treat the behavior of an array of atoms and the surface of the crystal.

If U is the surface potential energy per atom f the actual surface and  $U_0$  that of a perfectly flat surface, the surface roughness is defined as

Sr = 
$$(U-U_0)/U_0$$

The parameter Sr will clearly be zero per a perfectly flat surface and so a non zero value of Sr is a measure of the degree of roughness. A simple cubic array is treated and is assumed to be perfectly flat at absolute zero. The energy required to remove an atom from the perfectly flat surface and to place it on a site in the next layer (previously empty) is 2W<sub>B</sub>. Since, four bonds must be broken.

For temperatures well below critical value  $T_c S_r = 4exp(-2W_B/kT)$  in which the factor  $exp(-2W_B/kT)$  is the probability of excitation of a single atom from a full to an empty layer on the surface.

More recent treatments have predicted curves which differs markedly from that of Figure 1, but the trend is always from  $S_r = 0$  at low temperatures with the roughness increasing rapidly as T is raised above the some value in the region of  $0.2W_B/k$ . the temperature  $T_C$  at which the surface in contact either the vapor becomes ideally rough is given by  $W_B/k \ln(2-1)^{-1}$  and is normally much higher than the melting point of the solid.

For solid liquid interfaces  $W_B$  is lower and the surface may be rough at or below the melting point.

The parameter  $\alpha = (L/kT)^* f_k$ , where L—latent heat of the process, and  $f_k < 1$  is a crystallographic factor representing the fraction of all first neighbors lying in a plain parallel to the face considered. For  $\alpha < 2$ , the free energy is a minimum. When x= 0.5, that is when the surface is rough. For  $\alpha >> 2$ , the free energy is a minimum when x has a value close to 0 or 1, i.e., when the surface is almost smooth. Free energy reduction only occurs for a relatively smooth surfaces

c <17, or x > 99% for materials with large  $\alpha$  factors (e.g. Organics or polymers) whilst for low  $\alpha$  factors (e.g. metals) the maximum free energy reduction occurs for x= 50%

The Kossel, Stranski, Volmer(KSV) theory:

The importance of the surface discontinuous as nucleation cites was first recognized by Kossel, Stranski and Volmer(1939).

- The maximum binding energy between ad atom and the existing crystal lattice occurs for incorporation at a kink in a surface ledge
- The concept of crystal growth mechanism based on the existence of absorbed layer of solute atoms or molecules on a crystal face was first suggested by Volmer.
- When units of the crystallizing substance arrive at the crystal face they are not immediately integrated into the lattice, but merely lose one degree of freedom and are free to migrate over the crystal face.
- The thickness of the adsorption layers probably does not exceed 10nm.
- Atoms, ions or Molecules will link into the lattice in positions where attractive. Forces are greatest i.e., at the active centers and under ideal conditions this step wise build up will continue until the whole plane face is completed.

Before the crystal face can continue to grow ,i.e., before further layer can commence ,a' center of crystallization must come into the existence on the plane surface , and in the Gibbs-Volmer theory it is suggested that a mono layer island nucleus, usually called a two dimensional nucleus, is created.

The overall excess free energy of a nucleation may be written as

$$\Delta G = a\sigma + V \Delta G_V \tag{1}$$

Where a and V are the area and Volume of the nucleus, and if this is a circular disc of radius r and height h, then

$$\Delta G = 2\pi r h \sigma + \pi r^2 h \Delta G_V \tag{2}$$

And maximizing to find the critical  $six, r_c$ ,

$$\frac{d\Delta G}{dr} = 2\pi h\sigma + 2\pi r h\Delta G_V \tag{3}$$

Unit – I	V	
Singular and	Rough	Surfaces

	σ	
$r_{a} = -$		(4)
L	$\Delta G_V$	

Where  $\Delta G_{v}$  is a negative quantity

$$\Delta G_{crit} = \frac{\pi h \sigma^2 V}{KT lns} \tag{5}$$

The rate of two-dimensional nucleation can be expressed in the form of Arrhenius reaction velocity equation:

$$J' = B \exp(-\Delta G_{\frac{crit}{KT}})$$
(6)

It can be seen from the above equations that the ratio of the energy requirements of three to two dimensional nucleation (sphere:disc) is  $16\sigma V/3hKTlnS$ 

Kossel considered the crystal growth from atomistic considerations rather than thermodynamic functions.

Kossel considered the crystal growth from atomistic considerations rather than thermodynamic functions.

He assumed that a crystal is in equilibrium with its solution when it is just saturated. Also the attachment energy of a growth unit on a growing surface is a simple function of distance only.

In the case of homo polar crystals the attachment energy is due to Vander Waals forces and in the Ionic crystals (hetero polar) the attachment energy is due to electro static forces

Therefore from the Figs. 2a and 2b, it can be understood that the force experienced by the growth unit which is just occupying the growth surface, is the half of that well inside the crystal. For this reason, the growing crystal according to Kossel is treated as half-crystal. The attachment energy associated with a growing unit can be split up into three portions.

Thus the attachment energy (or lattice energy) of a given step can be symbolically written as

$$\phi = \phi' + \phi'' + \phi'''$$

(7)

When a single growth unit sits on a flat surface the energy released by the growth unit due to the attachment on the surface is due to a lone as shown in fig4a

When another growth unit sits adjacent to the previous unit as shown in fig 4b the energy released by the unit is correspondingly the component is due to the side pull when a growth unit sits on a row already begun (fig4c), the energy associated will be  $\phi = \phi' + \phi'' + \phi'''$ 

The energies associated with the growth units on the position depositions of a cubic crystal can be evaluated easily in terms of  $\phi'$ ,  $\phi''$  and  $\phi'''$ 

#### Conclusions

According to Kossel mode, growth of a crystal is a discrete process and not a continuous process. A new layer on a perfectly flat face will start growing from in interior of the face In the case of hetero polar (ionic) crystals Kossel was able to calculated the attachment energies on the basis of electrostatic forces and proved that the probability of starting a new surface is favored at the corners than at the edges mid-face is last favored.

Stranski considered that the most important quantity determining the growth process was the work necessary to detach a growth unit, i.e., to remove it from its position on the crystal surface is infinity.

The Kossel model and its dependence on surface nucleation, is unreasonable for the growth at moderate to low super saturation.

## The Burton, Cabrera and Frank (BCF) Theory

The points of dislocations with screw components (screw dislocations) at the crystal surfaces are important because they can provide a continuous source of steps (surface edges) which can propagate across the surface of the crystal and a theory of crystal growth including the mechanism of step generation and of transport into the step was given by (BCF) in 1951.

The velocity of the growth will depend on the shape of the growth spiral.

BCF used an equation for an Archimedean spiral

$$r = 2r_s^*\theta$$

(8)

Where r and  $\theta$  are the coordinates of any point on the spiral as indicated and  $r_s^*$  is the radius of the critical nucleus and is expressed as

## $r_s^* = \gamma_m a / KT\sigma$

Where  $\gamma_m$  is the free energy in terms of the energy per growth unit on the edge of the cylindrical nucleus and  $\gamma_m=a\gamma_e$ .  $\gamma_e$  is the edge free energy per unit length of the nucleus, a is the height corresponding to one growth unit (e.g. an atom or molecule)& $\sigma$  is the super saturation.

The distance yo between the steps of the spiral will thus be

$$y_o = 2r_s^* [(\theta + 2\pi) - \theta] = 4\pi r_s^*$$
(9)

A more rigorous approach by Carbera and Levine (1956) showed that a better approximation is given by

$$y_{o} = 19r_{s}^{*} = \frac{19\gamma_{m}}{KT\sigma}a$$
(10)

This approximation is used in the latter developments.

The second part of the BCF theory is concerned with the transport of the molecules from the bulk of the solution to kinks in the steps of the spiral.

The steps in the spiral are assumed to move negligibly slowly compared with the rate of migration of molecules on the surface. For example, the distance from the spiral centre is taken to be so large that curvature of the steps may be neglected. The net flux of the particles into the strip of the width dy on the surface in the region of a step will depends upon the flux  $J_v$  from the solution to the surface and on the flux  $J_s$  across the surface into step due to the concentration gradient by integration of molecules in to the surface at the step.

In the steady state the fluxes will balance & so for unit length in the X-direction,

$$\frac{dj_s(y)}{dy} - j_v = 0 \tag{11}$$

The surface flux js can be expressed in terms of the surface-diffusion coefficient and the local surface diffusion coefficient  $D_s$  and the local surface concentration  $n_s$  as

$$j_s = -D_s \frac{dn_s}{dy} = -D_s \frac{d}{dy} (n_{se}\sigma_s + n_{se}) = -D_s n_{se} \frac{d\sigma_s}{dy}$$
(12)

Where nse is the equilibrium concentration at the surface far from a step and  $\sigma$ s is the local value of the real-time super saturation.

Variable  $\psi$  as the difference between the surface super saturation  $\sigma s$  & the super saturation very far from a step ( $\sigma$ ) which is governed by the solute concentration in the bulk of the solution , thus

$$\psi = \sigma - \sigma_{s(y)} \tag{13}$$

And since  $\sigma$  is independent of y,

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$$j_s = D_s n_{se} \frac{d}{dy} (\sigma - \sigma_s) = D_s n_{se} \frac{d\psi}{dy}$$
(14)

The flux  $j_v$  can be written as the difference between the flux leaving the surface  $\psi \psi n_s(y)$  / desorption and that moving towards the surface  $n_{se}/\tau_{desorption}$  where  $\tau_{desorption}$  is the relaxation time governing desorption of solute from the surface, thus

$$j_{\nu} = \frac{\sigma n_{se} - n_s}{\tau_{desorption}} = \frac{n_{se}(\sigma - \sigma_s)}{\tau_{desorption}} = \frac{n_{se\psi}}{\tau_{desorption}}$$
(15)

On substitution of Eq. 7 & Eq. 8 into Eq. 4, the differential equation of solute transport becomes.

$$D_s \tau_{Desorption} \frac{d^2 \psi}{dy^2} = \psi \tag{16}$$

Or

$$y_s^2 \frac{d^2 \psi}{dy^2} = \psi \tag{17}$$

- i) Transport of solute
- ii) Diffusion through a boundary layer
- iii) Adsorption, on the crystal surface
- iv) Diffusion over the surface
- v) Attachment to a step
- vi) Integration into the crystal at a link.

Where  $y_s=(Ds \tau desorption)$  is the mean distance travelled by solute molecules on the surface. Eqn.10 has a general solution.

$$\psi = Aexp\left(\frac{y}{y_s}\right) + Bexp\left(\frac{-y}{y_s}\right)$$
(18)

And it is necessary to introduce boundary conditions to obtain values for A & B. The most probable situation is the  $ys>x_0$ , where xo is the average distance between kinks in a step.

For a set of equidistant steps of separation yo & with the origin of y chosen to be mid-way between the steps, the boundary condition may be expressed by putting the value of  $\psi$  at a step as  $_{\beta}\sigma$ , so that  $\psi =_{\beta}\sigma = Aexp(-\frac{y_0}{2y_s}) + Bexp(-\frac{y_0}{2y_s})$  when  $y = \pm 1/2$  yo, and  $\psi =_{\beta}\sigma = Aexp(-\frac{y_0}{2y_s}) + Bexp(\frac{y_0}{2y_s})$  for which A=B, and substitution in terms of  $_{\beta}\sigma$  Then from the eqn, 11, gives

$$\psi = \frac{\beta\sigma\cosh(y/y_s)}{\cosh\left(\frac{y}{2y_s}\right)} \tag{19}$$

If x0>>ys, it is necessary to introduce an extra factor co into eqn12 to take into account the non-planar diffusion fields around the kinks.

From eng.5, the flux of particles towards a step may now be written as,

$$J_s = D_s n_{se} \frac{d\psi}{dy} = \frac{D_s n_{se\,\beta\sigma}}{y_s} \frac{\sinh(^{y}/y_s)}{\cosh(^{y_0}/2y_s)}$$
(20)

If  $n_{se}$  is measured in gcm<sup>-2</sup>,  $j_s$  represents the flux in gcm<sup>-1</sup>s<sup>-1</sup> towards a step either of monomolecular or large height.

The linear rate of advance of step  $v_{st}$  is obtained by multiplying  $J_s$  is by the area  $\frac{1}{\rho a}$  per unit mass of the crystal so that, for a step of monoatonic height,

$$v_{st} = 2j_s \left( y = \frac{y_0}{2} \right) \frac{1}{\rho a} = \frac{2D_s n_{se} \beta \sigma}{9\rho y_s} tanh \frac{y_0}{2y_s}$$
(21)

The factor 2 is introduced since molecules enter the step from two sides.

In order to calculate the linear growth rate v of the crystal (in the Z direction), it is necessary to multiply the flux of steps by the height of a step.

For a step separation  $y_0$ , the number of steps per unit length is  $1/y_0$  and so the flux of steps in the y dissection will be  $v_{st}/y_0$ . If the step height is a the rate of growth will then be

$$v = \frac{v_{st}}{y_0}a\tag{22}$$

Or on substituting for  $V_{st}$ &y<sub>0</sub> from Eqs.14 and Eq. 3

$$V = \frac{2D_s n_{se} \beta \sigma KT}{19 \gamma_m \gamma_s \rho a} \tanh \frac{y_0}{2y_s}$$
(23)

If a parameter  $\sigma_1$  is defined as

$$\sigma_1 = \frac{\sigma_{y_0}}{2y_s} = \frac{9.5\gamma_m a}{\kappa T y_s} \tag{24}$$

Eqn 16 may be rewritten in the form of

$$v = \frac{D_s n_{se} \beta}{y_s^2 \rho} \frac{\sigma^2}{\sigma_1} \tanh \frac{\sigma_1}{\sigma} = \frac{C \sigma^2}{\sigma_1} \tanh \frac{\sigma_1}{\sigma}$$
(25)

The variation of growth rate with super saturation thus depends, on two parameters:  $c(=D_s n_{se}\beta/y_s^2\rho$ Which determines the absolute value of  $v_1 \& \sigma_1$  which determines the shape of  $v(\sigma)$  curve,

For low values of  $\sigma(\sigma << \sigma_1)$  Eq. 18 may be approximated by

$$V \cong \frac{C\sigma^2(exp2\sigma_1/\sigma)}{\sigma_1(exp2\sigma_1/\sigma)} \cong \frac{C\sigma^2}{\sigma_1}$$
(26)

While for  $\sigma > \sigma_1$ 

$$V \cong \frac{\mathcal{C}\sigma^{2}[(1+(2\sigma_{1}/\sigma)+\cdots)-1]}{\sigma_{1}[(1+(2\sigma_{1}/\sigma)+\cdots)+1]} \cong \mathcal{C}\sigma$$
(27)

The BCF theory therefore predicts a quadratic  $v(\sigma)$  curve for low values of the super saturation with a gradual transition to a linear law as the super saturations is increased above a critical value  $\sigma_1$ 

A relatively large value of  $\sigma_1$ , for a given material should result in a quadratic growth curve white a linear v( $\sigma$ ) plot should be expected according to the above theory if  $\sigma_1$ , is low

Cabra & coleman (1963) have pointed out that at higher super saturations, near the centre of the spiral may be lower than because of the depletion caused by surface diffusion to that portion of the spiral where the step spacing  $y_0$  is small. The result is that  $y_0$  decreases more slowly with  $\sigma$  predicted by Eq.3

This "back stress" effect makes the transition from a quadratic to a linear law occur at higher values of hen predicted by Eqs. 19 and 20 and a perfectly linear law is unlikely over any wide range of super saturation values

#### BCF theory of solution growth

In the case of solution growth, the molecules were assumed to enter the kinks directly rates than by entering an adsorption layer and undergoing surface diffusion.

The justification for this assumption was that the coefficient of volume diffusion ( $\sim 10^{-5}$  cm<sup>2</sup>s<sup>-1</sup>) is normally much higher than the coefficient of surface diffusion ( $\sim 10^{-8}$  cm<sup>2</sup>s<sup>-1</sup>) for molecules in solution so that any diffusion in a direction parallel to the crystal surface might be expected to occur in the boundary layer.

If the rate of flow of solute molecules to the kink s is governed by diffusion through the boundary layer, the net flux reaching the step s, which governs their rate of advance  $v_{st}$ , will be proportional to the super saturation  $\sigma_0$  with  $\frac{1}{y_0} \propto \sigma$  according to the eqn $(y_0 \cong 19\gamma_s^* = \frac{19\gamma_m a}{KT\sigma})$  The growth rate v will again vary as since  $(v=v_{st}a/y_o)$ . BCF considerate solute flow towards a kink in a hemispherical diffusion field and obtained an expression for the step velocity

$$V_{st} = \frac{D_{ne} 2\pi\sigma}{\rho X_0} \left[ 1 + \frac{2\pi a(\delta - y_0)}{x_0 y_0} + \frac{2a}{x_0} ln \frac{y_0}{x_0}^{-1} \right]$$

For low super saturation  $y_0$  is large and the third term in the bracket is the dominant one. In this case,  $v_{st}$  and q quadratic law Is predicted using eqn $\left[v = \frac{v_{st}a}{y_0}\right]$  since  $y_0\alpha\frac{1}{\sigma}$ .

However, at high super saturations the second term is dominant since  $y_0$  becomes small in the latter case

$$V_{st} \cong \frac{Dn_e \sigma y_o}{\rho a(\delta - y_0)}$$

And neglecting  $y_0$  in comparison with  $\delta$ , eqn $\left[v = \frac{V_{st}a}{y_0}\right]$  since  $y_0 \alpha \frac{1}{\sigma}$ 

Gives the growth rate a<sub>s</sub>

 $V = \frac{Dn_e\sigma}{\delta\rho}$ 

This case is exactly the same value-diffusion limited situation which was considered by Nernst.

#### Periodic Bond chain theory

The morphology of a crystal depends on the growth rates of the different crystallographic faces. Some faces growth form: the ones that have most influence are slow growing faces.

The growth of a given face is governed by the crystal structure and defects on the one hand, and by the environmental conditions o the other. A number of attempts have been made to predict the equilibrium growth form of crystal. According to the Bravais rule, the important faces governing the crystal morphology are those with the highest reticular densities and the greatest inter planner distance s, dnk1. Or in simpler terms, the slowest growing and most influential faces are the closest-packed and have lowest miller indices.

Faces at different orientation (i.e., different miller indices) have different surface structure. Atomically flat faces such as (100) face of a simple cubic structure, do not show steps under idea) conditions.

Ideal faces other than the singular ones show various degrees of ledge density, depending on their orientation. Faces differing by small angles from singular faces are called vicinal faces. Here the faces contain large segments of singular faces interrupted by monatomic steps, which increased with increasing angle from the singular faces, are called nonsingular faces.

The steps of nonsingular faces show a large number of kinks and hence these faces have a rough surface structure.

In the extreme case, it is also possible that the interface extends over large distances into the medium and it is difficult to pinpoint its position precisely. Such interfaces are called diffuse interfaces.

The surface energy of crystals is usually anisotropic because it depends on the density of steps i.e., on the crystallographic orientation. For a singular face surface energy has a sharp minimum, while for a nonsingular face, it is the highest

The Gibbs-Curie-Wulff surface energy theory of crystal growth suggests that the form or equilibrium shape should be such that the crystal has a minimum total surface free energy per unit volume.

Hartmann (1973) who classified crystal surfaces into F(flat), S(stepped) and K(Kinked) faces in terms of the number of uninterrupted chain of strong bonds in a layer of thickness  $d_{hx}$ ). The uninterrupted chains of strong bonds are called periodic Bond Chains (PBC)

The figure has a flat or F face with strong bonds linking neighboring PBC's and figure b has a stepped or  $\delta$  face since these bonds are not directed along the surface.



A section of crystal with O representing a PBC

(a) Neighboring PBC s linked by strong bonds

(b) Neighboring PBC s not linked by strong bonds along the S face

An F face contains two or more PBCs, an S face contains only one PBC, while a K face contains no PBC n the layer.

In ideal conditions, F faces are atomically flat, S faces are composed of ledges and K faces are composed of kinks only. Obviously, in terms of the above classification, F face S correspond to singular face S, S faces with a small density of ledges t vicinal face S, and K face S correspond to nonsingular faces. A natural consequence of the structure of surface S is that F face S are the slowest growing Faces S, S face grow at a faster rate than the F face S, & K face S are the fastest growing face S and are usually absent in the growth morphology.

Microscopically, F faces remain smooth, while S faces show parallel striations which appear to start from one of the neighboring F face S.

Faces endowed with strong PBC s are morphologically more important than those having relatively weak PBC s, This nature of the face S is due to the fact that the weaker the PBC, the higher the density of kinks it can provide by edge nucleation and statistical fluctuations Bennema and Gilmer (1973) defined the change in Gibbs free energy g resulting from the roughening of a flat reference plane according to the relationship.

$$\frac{\Delta G}{NKT} = \beta \left[ \sum_{n=\alpha}^{0} (1 - c_n) - \sum_{n=1}^{\alpha} C_n \right] + \alpha \sum_{n=-\alpha}^{\alpha} C_n (1 - C_n) + \sum_{n=-\alpha}^{\alpha} (c_n - C_{n+1}) \ln(C_n - C_{n+1}) \right]$$
  
where  $\beta = \frac{\Delta \mu}{KT}$  and  $\alpha = \frac{4\epsilon}{KT}$ 

 $C_n$  is the concentration of sites in the nth atomic layer from the flat reference plane which still have solid-solid bonds, $\Delta \mu$  is the chemical potential difference between solid & fluid,  $\epsilon$  is the energy gain accompanying the replacement of a solid-solid bond by a solid-fluid bond, I,e., roughening)

In a field where the value  $\alpha$  is high and the inter atomic bonding forces are large, it is difficult to create rough surfaces and the layer-growth mechanism predominates even for a relatively high chemical or thermal driving force  $\Delta\mu$ 

Where  $\alpha$  is low, however (or for moderate  $\alpha$  values under conditions of high super saturation) the flat surfaces unstable, is readily roughened and growth occurs by a continuous random a atom absorption mechanism (Field B)

This analysis, therefore, confirms the intuitive reasoning that the roughening transitions would be dependent upon both the driving forces for the reaction (the chemical & thermal driving forces are taken together as  $\Delta \mu$ ) and the bond strength in the interface region.

# **GROWTH FORM THE MELT**

Melt growth is the process of crystallization by fusion and resolidification of the pure material, crystallization form a melt on cooling the liquid below its freezing point. In this technique apart from possible contamination form crucible materials and surrounding atmosphere, no impurities are introduced into growth process and the rate of growth is normally much higher than that possible by other methods. Melt growth is commercially the most important method of the crystal growth. The growth from the melt can be further sub grouped into various techniques.

The main techniques are:

- 1. Bridge man technique.
- 2. Czochralski technique
- 3. Verneuil technique
- 4. Zone melting technique
- 5. Heat exchanger method
- 6. Skull melting
- 7. Shaped crystal growth.

The major practical factors to be considered during growth of crystals from melt are

- a. Volatility or dissociability
- b. The chemical reactivity and
- c. The melting point

## 1. The Bridge man technique

This technique was named after its inventor (Bridge man 1925, Stockbarger 1938). In this process the material to be grown is taken in a vertical cylindrical container, tapped conically with a point bottom and maid to melt using a suitable furnace. The container is lowered slowly from the hard zone of the furnace into the cold zone. The rates of the movement per such process is
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range from about 0.1 to 200mm per hour but are mostly in the range 1 to 30mm hour. Crystallization begins in the top and continues usually by growth from the first formed nuclease.

The relative advantage of the technique are low coast with the added advantage that the melt temperature increases with the distance from the solid liquid interface and the system is therefore density stable and less prone to convection affects than the Czocharalski technique. A disadvantage is that a low growth rates used typically 1-30mm per hour, mean that ht e melt is in contact with the container for long periods, increasing the risk of impurity pickup.

A second disadvantage is that adhesion of the solid materials to the ampoule wall or compression of a solid by the contracting container during cooling can lead to the development of stresses high enough to nucleate dislocations in the material.

A further drawback of the technique is that the container wall acts as a preferential spurious nucleation site, resulting in polycrystalline rather than single growth unless the temperature gradient and the liquid solid interface shape are well controlled.

The Bridge man technique cannot be used for the materials which decompose before melting or which undergo solid-state phase. Transformation between their melting points and the temperature to which they will be cooled. Figure 1 shows typical Bridge man technique configuration. Mechanically, Bridge man technique is used only fairly simple.



Fig. 13 Bridge man technique system

The necessary movements can be produced by using wires wound on by lead screws f the type used in machine tools. With the availability of wide range of AC or DC motors stepper motors, high torque, multistep micro motors and related electronics the rotation or translation can be achieved with out vibrations induced to the growth station. This method id best suited for low melting point materials.

### **Container selection.**

The following guidelines for container selection are applicable for both Bridge man and Czochralski process.

- 1. The most obvious desirable characteristics of a container is that its pressure should not contaminate the crystals.
- 2. The container should not react with the melt.
- 3. The container should have smaller coefficient of the thermal expansion than the crystal
- 4. The container should have smaller thermal conductivity than the crystal.
- Corrosion of crucibles is related to the wetting angle of melt.
   Graphite crucible is a useful container material for some covalently bound and metallic materials and it is widely used for ionic materials.

# **Crystal Pulling Technique.**

The Czochraski growth geometry is shown schematically in figure 2. The material to be grown is melted by induction or resistant heating under controlled atmosphere in a suitable non-reacting container. The melt temperature is adjusted to be slightly above the melting point and seed crystal is lowered to the melting surface.

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# Fig. 14 Czochraski growth geometry

After thermal equilibrium, the seed is contacted with the melt and the melt temperature is raised to establish the desired growth interface configuration by activating pulling mechanism the seed is withdrawn from the melt (with a simultaneous temperature adjustment) at such a rate that the crystal diameter is gradually increased to its desired value.

The growth interface in is configuration is expected to confirm at all the times, to the location and shape of the liquid meniscus (of the curvature and height h).

Growth at constant diameter is achieved by maintaining the solidification isotherm in a vertical position intersecting the meniscus at the point where the isotherm becomes perpendicular to the melt surface. This condition id maintained by adjustments of the following parameters the rate pulling, rate of liquid level drop.(determined by relative diameters of the crystal and crucible). The heat fluxes into and out the system, and to a lesser extend but seed and/or crucible rotation. Full diameter control is frequently achieved by automatic diameter control ((ADC) techniques) employing both analog and digital system.

#### Practice of the crystal beam

The precise growth procedure will vary according to the properties of the starting materials and crystal properties.

The general procedure after setting up the apparatus involves removing the air from the apparatus and conditioning the growth chamber environment with a suitable gas (or vacuum).

The seed crystal, which is generally a single crystal, will be aligned by a suitable mechanical design that ensures the desired seed orientation and confirms with the full rod axis. Having melted the charge and establish it precise melting relative to the thermocouple for temperature sensor the seed is rotated and lowered into the melt.

The speed is controlled to minimize thermal shock. Once temperature equilibrium is established and when the solid /liquid inter phase is just above the surface of the liquid pulling is commenced by suitable adjustment of power to melt (or the pull rate in certain circumstances) the seed can be pulled from the melt at a rate which matches the rate at which liquid crystallizes on the seed position. The position of the solid/liquid crystallizes on the seed. The position of the solid/liquid interface stays approximately constant.

The shape of the crystal is controlled by the angle of contact  $\theta$  of the meniscus with the crystal cylinder with  $\theta < 0$  greater than zero the crystal will narrow. When  $\theta = 0$  when the crystal will grow parallel and when  $\theta > 0$  the crystal will grow out by raising the power to the melt the slid/liquid interface raised above the melt and the surface tension forces waists in the liquid column leading  $\theta$  to be -ve.

Too radical change causes too great a weight of a liquid to be supported by he surface tension forces & the liquid pulls away & pasts from the seed.

In the reverse situation, the solid liquid interface moves to the surface of the liquid making  $\theta$  to increase beyond 90° & under extreme conditions the whole surface of the melt can be crystallized. The need for good visibility and precise control of the power to the melt is thus evident. A standard necking procedure is employed to initiate the growth of high quality dislocation free single crystals. The terminology necking means reducing the diameters gradually to grow as a very narrow thin long neck of 2-3 mm in diameter & hen the diameters is

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allowed to enlarge to the required size & maintained constant. The purpose of necking procedure can be two fold. By making a thin neck the dislocation density is drastically reduced in the seed & ultimately in the drastically reduced in the seed & ultimately in the growing crystal. This is probably the most important reason or necking. It enables single crystals to be prepared from multiple grained 'seeds'. The reduction in diameters significantly limits the number of different grains from which single crystal grins can be grown & amplified in size. Single crystal seed can then be selected out from the results of one or two propagation attempts. The termination of crystal growth run is also important.

Slow cool down and termination of the growth by necking may be required to reduce amount of thermal shock sustained by the crystal. The primary objective of crystal growth is the production of materials with predicted & controlled properties.

# **Controlling parameters**

# **Rate of pulling**

The average growth rate of a crystal is determined by the pulling rate & the radii of the crucible and the crystal

The radius of the crystal is however controlled by the melt temperature & the temperature gradient at the growing interface.

The rotation of the crystal causes a centrifugal flow on the liquid immediately adjacent to its surface.

The critical parameters, which determines the strength of convection of an ideal gas, is the Rayleigh number Ra

$$R_{a} = \frac{\Delta T}{T} = \frac{gd^{3}}{K_{0}\vartheta_{0}}$$

When  $\vartheta$  o=kinematic viscosity, ko=thermal diffusivity, d=depth of the convection cell, g=acceleration due to gravity.

 $\Delta T$  vertical temperature difference across call & p=gas pressure.

 $R_a$  depends on the temperature difference on the cell, & on the cube of d & the square of p. closely spaced baffling & low pressure can thus necessary for limiting gaseous convection.

#### **CONVECTION IN MELTS:**

When a melt is heated from below, the buoyancy forces generated cause the hotels, less dense liquid, to rise and the cooler liquid to fall, generating a convective flow. Convective flow may also result from the gradient of surface tension forces or gradient in solute or alloy concentration. The resulting flow patterns and their effect on temperature distribution have been studied extensively.

The important parameters governing the onset & nature of convection patterns in melts are the thermal characteristics of the material, the aspect ratio of me contains and imposed temperature gradients.

The Prandtl number  $N_{pr}$  is one of the most important factors governing the fluid flow patterns and is defined as the radio v/k, where v is he kinematic viscosity of the liquid k is the thermal diffusivity. It is dependent only on the thermal characteristics of the liquid and independent of contained geometry or applied temperature gradient.

In high Prandtl number systems ( $N_{pr}$ >>1) suck as oxides, strong fluid flow is largely confined to boundary layers regions. (Fig3 ) whereas in low Prandtl number materials such as metals & semiconductors the streamlines are more generally distributed throughout the bulk but stream velocities are much higher under high temperature gradients.

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Fig. 15 Contours with Prandtl number of 0.013 and 10

Fig. 15 stream – function contours generated in fluids with Prandtl number of 0.013 and 10 which are contained in square enclosures heated and cooled at vertical sides under an increasing horizontal temperature difference.

The temperature gradient provides the driving force for the convection. In horizontal systems this driving force is characterized by the Grashof number Gr where

# ${\rm Gr}=\alpha g l^4 \Delta T_H/\vartheta^2$

In which g is the gravitational constant,  $\alpha$ -the thermal expansion co-efficient of the melt,  $\Delta T_H$  is the imposed horizontal temperature difference over the length l separating the opposite boundaries of the melt and  $\uparrow \vartheta$  is the kinematic viscosity o the liquid.

In vertically driven convection systems, the relevant dimensionless number is he Rayleigh number Ra defined by

 $Ra = \frac{\propto g d^4 \Delta T_v}{9_K}$ 

Where  $\Delta T_{v}$  is the vertical temperature gradient.

As the Rayleigh (or Grashof number) increase with increase in  $\Delta T$ , the fluid flow begins to more by convective flow and further increases lead to progressive breakdown into smaller convection cells as shown in fig4

The onset of each mode is governed by a series o Eigen values  $Ra^{i,n}$  where i is the mode number and n the mode symmetry

In practice, only n=1 the asymmetric mode with flow up one side of the contains and down the other, or n=0 the axis symmetric mode, are of physical significance since Ra  $\alpha$  d<sup>4</sup>however, I can attain large values in cylindrical contains with large d/a aspect ratio, e.g. typical Bridgman growth ampoules.

Further increase I Ra or Gr leads to the development of instability in the flow pattern, usually taking the form of oscillatory motion of the convection cells within the melt, the oscillation frequency increasing as Ra increases



Fig. 16 convection cell formation as a function of increasing Rayleigh number

a) Ra=230 b) Ra=280 c) Ra=382

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# Unit – IV Singular and Rough Surfaces

# Origin and nature of convective process in the melt growth system

The basic melt flow in a non rotation growth system is a thermal convection shear flow generated by the imposed radial (horizontal) temperature gradient required for growth, In growth systems where the thermal centre coincides with the geometric centre of the crucible symmetric melt flow is established, where hot liquid rises at the crucible wall and moves radically inwards at the top surface to the cooler thermal center where it descends to the crucible bottom. The basic flow pattern is shown in Fig. 16

The exact pattern established is very sensitive to the boundary imposed on temperature and melt flow velocity, the melt aspect ratio (height to radius), the thermal and viscous properties of the liquid. The melt flow pattern believed predominantly established in to Chralski growth systems is indicated in fig6. The basic features with are important to crystal growth process, are

i) The non-uniform nature of the thermal convection flow at different points of the interface results, in a correspondingly non-uniform diffusion boundary layers of thickness SD & thus is responsible for radial variations in segregation at the freezing interface.

ii) The unsteady (time-dependent) behaviours of some thermal convection flows leads to temporal (transient) variations in R and 8 which in turn both generate compositional striations.

iii) The lack of coincidence between the thermal centre of symmetry and geometrical centre of the melt leads to a drifting of the growing crystal from its original position'

iv) The thermal convection flows may adversely affect the shape of the solidification isotherm (growth interface morphology)

HANG Symmetric Convection flow patterns . Them Fig.6. Thermal convection in Czychnalski melts-Axislimmetric Pattern S in Czachrolski metts Antisymmetric

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# Unit – IV Singular and Rough Surfaces

These features of thermal convection flow are undesirable and therefore make it necessary to provide control over melt flow velocities and temperature distributions at the growth interface by other means

# **POSSIBLE QUESTIONS**

# PART – B

1.Briefly explain the melt growth of oxide crystals for saw, piezoelectric and nonlinear optical applications

- 2.Explain the working of heat exchanger method with neat sketch
- 3.Explain Periodic bond chain theory
- 4. Explain crystal pulling technique
- 5. What are the salient features of the Miller Krumbhaar Model?
- 6. How the purity of the crystal is achieved by Zone melting technique
- 7.Write in detail about the Kossel, Stranski, Volmer (KSV) theory
- 8.Describe the principle and working of Bridgman technique

9.Explain the BCF theory of solution growth of crystals

10.Explain skull melting process with neat sketch

# PART – C

1.Explain in detail how single crystals are characterized using XRD technique and it is analysed

#### KARPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE-21

#### DEPARTMENT OF PHYSICS MSC PHYSICS (2017-2019) MATERIAL SCIENCE(17PHP105A) 2017-2018 (ODD) MULTIPLE CHOICE QUESTIONS Unit IV

Question	Option 1	Option 2	Option 3	Option 4	Answer
In Bridgman technique, the rates of movement are mostly in the range	1-30mm/hr	0.1-200mm/hr	200-300mm/hr	above 300mm/hr	1-30mm/hr
The advantages of the Bridgman technique are	low-cost	suitable for low melting point materials	adhesion of the solid materials to the ampoule wall	both a and b	both a and b
In Bridgman technique, the melt temperature	decreases	increases	increases or decreases	constant	increases
A disadvantage in Bridgman technique is	nucleate dislocations in the material	low-cost	adhesion of the solid materials to thee ampoule wall	both a and c	both a and c
The container wall acts as a preferential, spurious nucleation site, resulting in	polycrystalline growth	single crystal growth	amorphous growth	single or polycrystal growth	polycrystalline growth
The requirement that the freezing isotherm should move systematically through the molten charge can be satisfied by moving	the crucible	the furnace	changing the furnace temperature	any one of the above	any one of the above
The Bridgman technique cannot be used for materials which	decompose before melting	undergo solid state phase transformation	decompose after melting	both a and b	both a and b
Bridgman technique is best suited for	high melting point materials	high vapour pressure materials	low melting point materials	both high and low melting point materials	low melting point materials
The characteristic of a container	not react with the melt	smaller coefficient of thermal expansion than the crystal	smaller thermal conductivity than the crystal	all the above	all the above
The materials with covalently bound crystals are often compatible with containers made of	glasses	gold	silver	platinum	glasses
Graphite crucible is a useful container material for	ionic materials	some covalently bound materials	some metallic materials	all the above	all the above
which one of the following comes under crystal pulling technique	Bridgman	zone refining	skull melting	Czochralski	Czochralski
Which method can produce crystals, weighing from several grams to many kilograms	crystal pulling	zone melting	slow evaporation	chemical vapour deposition	crystal pulling
crystal growth is a complex process, which usually takes place by a	phase change	solid phase	liquid phase	vapour phase	phase change
Irregular convective flow in crystal pulling can be produced due to	higher temperature gradients	concentration gradients	high vapour pressure	both a and b	higher temperature gradients
The seed is withdrawn from the melt at such a rate that the crystal Is gradually increased to its desired value	length	weight	diameter	both length and diameter	diameter
Growth at constant diameter is maintained by adjustments of the	rate of pulling	rate of liquid level drop	heat fluxes into and out of the system	all the above	all the above
The seed can be pulled from the melt at a rate which matches the rate at which liquid crystallizes on the	seed	container	crystal	puller	seed

With angle of contact $\theta < 0$ the crystal will	narrow	parallel	grow out	either b or c	narrow
With angle of contact $\theta=0$ the crystal will	narrow	parallel	grow out	either a or c	parallel
With angle of contact $\theta > 0$ the crystal will	parallel	narrow	grow out	either a or b	grow out
The terminology necking means reducing the dia gradually to grow as a In diameter	2-3mm	10mm	40mm	0.5mm	2-3mm
The pull rod provides rotation and facility to lift and lower the crystal inmethod	Bridgman	czochralski	zone melting	both a and b	czochralski
The average growth rate can be obtained by equating the mass of the that has formed	solid	liquid	liquid or solid	solid and liquid	solid
The important parameter governing the onset and nature of convection pattern in melts	the thermal characteristics of the material	the aspect ratio of the container	the imposed temperature gradients	all the above	all the above
The Prandtl number is dependent only on the	contained geometry	applied temperature gradient	the thermal characteristics of the liquid	the aspect ratio of the container	the aspect ratio of the container
In high Prandtl number systems such as oxides, strong fluid flow is largely	distributed throughout the bulk	confined to boundary layer regions	confined to central regions	all the above	confined to boundary layer regions
In low Prandtl number materials such as metals and semiconductors the streamlines are more generally	confined to boundary layer regions	distributed throughout the bulk	confined to central regions	none of the above	distributed throughout the bulk
In horizontal systems the temperature gradient is characterised by the	Rayleigh number	Prandtl number	Grashof number	none of the above	Rayleigh number
In vertically driven convection systems, the relevant dimensionless number is the	Rayleigh number	Prandtl number	Grashof number	none of the above	Grashof number
The Prandtl number is defined as the ratio	ν/κ	QI/ĸ	VI/ĸ	v/D	ν/κ
The Prandtl number is defined as the ratio Rayleigh number Ra is defined by	$v/\kappa$ $\alpha g d^4 \Delta T_v / v \kappa$	$\frac{QI/\kappa}{\alpha gI^4 \Delta T_H/\nu^2}$	VI/κ ν/κ	ν/D VI/κ	$v/\kappa$ $\alpha g d^4 \Delta T_v / v \kappa$
The Prandtl number is defined as the ratio Rayleigh number Ra is defined by Grashof number Gr is defined by	$v/\kappa$ $\alpha g d^4 \Delta T_v / v \kappa$ $v/\kappa$	$QI/\kappa$ $\alpha gI^4 \Delta T_H/v^2$ $\alpha gd^4 \Delta T_v/v\kappa$	$VI/\kappa$ $v/\kappa$ $agI^4\Delta T_H/v^2$	v/D VI/ĸ v/D	$v/\kappa$ $agd^4\Delta T_v/v\kappa$ $agI^4\Delta T_H/v^2$
The Prandtl number is defined as the ratio Rayleigh number Ra is defined by Grashof number Gr is defined by As the Rayleigh(or Grashof number) increases with increase in , the fluid flow begins to move by convective flow	$\frac{\nu/\kappa}{\alpha g d^4 \Delta T_{\nu}/\nu \kappa}$ $\nu/\kappa$ $\Delta T$	$\frac{QI/\kappa}{\alpha gI^4 \Delta T_H/\nu^2}$ $\frac{\alpha gd^4 \Delta T_v/\nu \kappa}{\nu}$	$\frac{VI/\kappa}{\nu/\kappa} \\ \alpha g I^4 \Delta T_{\rm H} / \nu^2 \\ \alpha g I^4 \Delta T_{\rm H} / \nu^2 \\ \end{array}$	v/D VI/ $\kappa$ v/D both a and b	$\frac{\nu/\kappa}{\alpha g d^4 \Delta T_{\nu} / \nu \kappa} \\ \frac{\alpha g l^4 \Delta T_H / \nu^2}{\Delta T}$
The Prandtl number is defined as the ratio Rayleigh number Ra is defined by Grashof number Gr is defined by As the Rayleigh(or Grashof number) increases with increase in , the fluid flow begins to move by convective flow Typical Bridgman growth ampoules haveaspect ratio	$ \frac{\nu/\kappa}{\alpha g d^4 \Delta T_{\nu}/\nu \kappa} $ $ \frac{\Delta T}{\alpha g d^4 a} $ large d/a	$\begin{array}{c} QI/\kappa \\ \alpha gI^4 \Delta T_H/\nu^2 \\ \alpha gd^4 \Delta T_\nu/\nu \kappa \\ \nu \\ small d/a \end{array}$	$\frac{VI/\kappa}{\nu/\kappa}$ $\alpha gI^4 \Delta T_H / \nu^2$ $\alpha gI^4 \Delta T_H / \nu^2$ large or small d/a	v/D VI/ $\kappa$ v/D both a and b none of the above	$v/\kappa$ $\alpha g d^4 \Delta T_v/v\kappa$ $\alpha g I^4 \Delta T_H/v^2$ $\Delta T$ large d/a
The Prandtl number is defined as the ratio Rayleigh number Ra is defined by Grashof number Gr is defined by As the Rayleigh(or Grashof number) increases with increase in , the fluid flow begins to move by convective flow Typical Bridgman growth ampoules haveaspect ratio Forced convection flow patterns in Czochralski melts are due to various combinations of	$ \frac{\nu/\kappa}{\alpha g d^4 \Delta T_{\nu}/\nu \kappa} $ $ \frac{\nu/\kappa}{\Delta T} $ large d/a crystal rotation	$\frac{QI/\kappa}{\alpha gI^4 \Delta T_H/v^2}$ $\frac{\alpha gd^4 \Delta T_v/v\kappa}{v}$ small d/a seed rotation	$\frac{VI/\kappa}{\nu/\kappa}$ $\alpha gI^4 \Delta T_H / \nu^2$ $\alpha gI^4 \Delta T_H / \nu^2$ large or small d/a crucible rotation	v/D VI/ĸ v/D both a and b none of the above seed rotation and crucible rotation	$\frac{v/\kappa}{\alpha g d^4 \Delta T_v/v\kappa}$ $\frac{\alpha g l^4 \Delta T_H/v^2}{\Delta T}$ $\frac{\Delta T}{\alpha g d/a}$ seed rotation and crucible rotation
The Prandtl number is defined as the ratio Rayleigh number Ra is defined by Grashof number Gr is defined by As the Rayleigh(or Grashof number) increases with increase in , the fluid flow begins to move by convective flow Typical Bridgman growth ampoules haveaspect ratio Forced convection flow patterns in Czochralski melts are due to various combinations of The shape of the growth surface is dependent upon its	v/κ $agd^4 \Delta T_v/v κ$ v/κ $\Delta T$ large d/a crystal rotation crystallographic orientation	$\begin{array}{l} QI/\kappa \\ \alpha gI^4 \Delta T_H/\nu^2 \\ \alpha gd^4 \Delta T_\nu/\nu \kappa \\ \nu \\ \text{small d/a} \\ \text{seed rotation} \\ \text{local temperature gradient} \end{array}$	$\frac{VI/\kappa}{\nu/\kappa}$ $\alpha gI^4 \Delta T_H/\nu^2$ $\alpha gI^4 \Delta T_H/\nu^2$ large or small d/a crucible rotation both a and b	v/D VI/ĸ v/D both a and b none of the above seed rotation and crucible rotation none of the above	$v/\kappa$ $\alpha g d^4 \Delta T_v / v \kappa$ $\alpha g I^4 \Delta T_H / v^2$ $\Delta T$ large d/a seed rotation and crucible rotation both a and b
The Prandtl number is defined as the ratio Rayleigh number Ra is defined by Grashof number Gr is defined by As the Rayleigh(or Grashof number) increases with increase in , the fluid flow begins to move by convective flow Typical Bridgman growth ampoules haveaspect ratio Forced convection flow patterns in Czochralski melts are due to various combinations of The shape of the growth surface is dependent upon its The simplest and the best case from the point of view of good quality growth is the	v/κ $agd^4 \Delta T_v/v κ$ v/κ $\Delta T$ large d/a crystal rotation crystallographic orientation concave interface	QI/ $\kappa$ $\alpha$ gI <sup>4</sup> $\Delta$ T <sub>H</sub> / $\nu^2$ $\alpha$ gd <sup>4</sup> $\Delta$ T <sub>v</sub> / $\nu$ $\kappa$ $\nu$ small d/a seed rotation local temperature gradient convex interface	VI/ $\kappa$ $\nu/\kappa$ $\alpha g I^4 \Delta T_H / \nu^2$ $\alpha g I^4 \Delta T_H / \nu^2$ large or small d/a crucible rotation both a and b planar interface	v/D VI/κ v/D both a and b none of the above seed rotation and crucible rotation none of the above both a and c	$v/\kappa$ $\alpha g d^4 \Delta T_v / v \kappa$ $\alpha g l^4 \Delta T_H / v^2$ $\Delta T$ large d/a seed rotation and crucible rotation both a and b planar interface
The Prandtl number is defined as the ratio Rayleigh number Ra is defined by Grashof number Gr is defined by As the Rayleigh(or Grashof number) increases with increase in , the fluid flow begins to move by convective flow Typical Bridgman growth ampoules haveaspect ratio Forced convection flow patterns in Czochralski melts are due to various combinations of The shape of the growth surface is dependent upon its The simplest and the best case from the point of view of good quality growth is the Which model calculates, for a given instant of growth, the global heat transfer, the shape of the solid-liquid interface, natural and forced convection		QI/ $\kappa$ $\alpha gI^4 \Delta T_H / v^2$ $\alpha gd^4 \Delta T_v / v \kappa$ v small d/a seed rotation local temperature gradient convex interface Time dependent model with unknown crystal shape	VI/ $\kappa$ $v/\kappa$ $\alpha g I^4 \Delta T_H / v^2$ $\alpha g I^4 \Delta T_H / v^2$ large or small d/a crucible rotation both a and b planar interface Quasi-steady state model	v/D VI/ĸ v/D both a and b none of the above seed rotation and crucible rotation none of the above both a and c both a and c	$v/\kappa$ $\alpha g d^4 \Delta T_v / v \kappa$ $\alpha g l^4 \Delta T_H / v^2$ $\Delta T$ large d/a seed rotation and crucible rotation both a and b planar interface Quasi-steady state model
The Prandtl number is defined as the ratio Rayleigh number Ra is defined by Grashof number Gr is defined by As the Rayleigh(or Grashof number) increases with increase in , the fluid flow begins to move by convective flow Typical Bridgman growth ampoules haveaspect ratio Forced convection flow patterns in Czochralski melts are due to various combinations of The shape of the growth surface is dependent upon its The simplest and the best case from the point of view of good quality growth is the Which model calculates, for a given instant of growth, the global heat transfer, the shape of the solid-liquid interface, natural and forced convection The model calculates, as functions of time		QI/ $\kappa$ $\alpha gI^4 \Delta T_H / v^2$ $\alpha gd^4 \Delta T_v / v\kappa$ v small d/a seed rotation local temperature gradient convex interface Time dependent model with unknown crystal shape Time dependent model with unknown crystal shape	VI/ $\kappa$ v/ $\kappa$ $\alpha g I^4 \Delta T_H / v^2$ $\alpha g I^4 \Delta T_H / v^2$ large or small d/a crucible rotation both a and b planar interface Quasi-steady state model Quasi-steady state model	v/D VI/x v/D both a and b none of the above seed rotation and crucible rotation none of the above both a and c both a and c both a and b	$v/\kappa$ $\alpha g d^4 \Delta T_v / v \kappa$ $\alpha g l^4 \Delta T_H / v^2$ $\Delta T$ large d/a seed rotation and crucible rotation both a and b planar interface Quasi-steady state model both a and b
The Prandtl number is defined as the ratio Rayleigh number Ra is defined by Grashof number Gr is defined by As the Rayleigh(or Grashof number) increases with increase in , the fluid flow begins to move by convective flow Typical Bridgman growth ampoules haveaspect ratio Forced convection flow patterns in Czochralski melts are due to various combinations of The shape of the growth surface is dependent upon its The simplest and the best case from the point of view of good quality growth is the Which model calculates, for a given instant of growth, the global heat transfer, the shape of the solid-liquid interface, natural and forced convection The model calculates, as functions of time In Model, the variation of the tri-junction radius as a function of time is calculated		$\begin{array}{l} QI/\kappa \\ \alpha gI^4 \Delta T_H/v^2 \\ \alpha gd^4 \Delta T_v/v\kappa \\ v \\ small d/a \\ seed rotation \\ local temperature gradient \\ convex interface \\ Time dependent model \\ with unknown crystal \\ shape \\ Time dependent model \\ with unknown crystal \\ shape \\ Time dependent model \\ with unknown crystal \\ shape \\ Time dependent model \\ with imposed crystal \\ shape \\ \end{array}$	VI/ $\kappa$ v/ $\kappa$ $\alpha g I^4 \Delta T_H / v^2$ $\alpha g I^4 \Delta T_H / v^2$ large or small d/a crucible rotation both a and b planar interface Quasi-steady state model Quasi-steady state model Time dependent model with unknown crystal shape	<pre>v/D VI/k V/D both a and b none of the above seed rotation and crucible rotation none of the above both a and c both a and c both a and c both a and b</pre>	v/κ $agd^4 \Delta T_v/v κ$ $agI^4 \Delta T_H/v^2$ $\Delta T$ large d/a seed rotation and crucible rotation both a and b planar interface Quasi-steady state model both a and b Time dependent model with unknown crystal shape

The Czochralski system for the growth of oxides incorporates an induction heating system operating at	455kHz	455Hz	1kHz	100Hz	455kHz
and, are two ferroelectric oxides	Lithium niobate and Ti:Al <sub>2</sub> O <sub>3</sub>	Lithium niobate and Lithium tantalate	BGO and Lithium niobate	Aluminium and iron oxide	Lithium niobate and Lithium tantalate
Lithium niobate and Lithium tantalate have been widely investigated due to an	piezoelectricity	pyroelectricity	electro-optic property	all the above	all the above
Equilibrium referes to a growth speed of	0mm/min	10mm/min	2mm/min	none of these	0mm/min
Lithium niobate and Lithium tantalate crystals are	biaxial crystals	uniaxial crystals	symmetric crystals	none of the above	uniaxial crystals
Lithium tantalate and Lithium niobate crystals are used for	laser systems	surface acoustic wave	magnetic bubble devices	optical components	surface acoustic wave
A good ratio between the crucible diameter and the crystal diameter is	1	2	10	3	2
The size of the crystal is limited by the	size of the crucible	thermal gradients in the crystallization area	pull rate	both a and b	size of the crucible
crystal has been studied extensively for acoustic wave devices	Lithium niobate	Nd:YAG	ҮАР	langasite	langasite
Isomorphic crystals have	zero temperature coefficient	large electromechanical coupling factor	congruent melting point	all the above	all the above
Dissociable compounds can be grown by	CZ method	sealed tube methods	vertical pulling methods	both b and c	both b and c
Pick out the suitable property of encapsulant	melt after the compound melts	more dense than the melt of the compound	transparent	not wet the crucible	transparent
Boron tri oxide has proved to be one of the best encapsulants fortype melts	metals	semiconductor	insulator	both a and b	both a and b
The technological importance of GaAs and InP comes about because of their use in	electronic devices	photonic devices	magnetic devices	both a and b	both a and b
The paper published by Pfann(1952) was related to Technique	Zone melting	Zone refining	float zone	all the above	all the above
In zone refining, if freezing is rapid enough, k may actually	approach unity	less than unity	more than unity	0 to 1	approach unity
process is used for the growth of zirconium oxide	Zone melting	Skull melting	CZ	both a abd c	Skull melting
is a process, which dynamically controls both the heat input and the heat extraction in a crystal growth furnace	Skull melting	Zone melting	Bridgman	Heat exchanger	Heat exchanger

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Nanotechnology: An introduction – Nanodevices – Carbon nanotubes – Types of Carbon Nanotubes: Single walled, Multiwalled, Torus – Properties: Hardness – Strength – Electrical – Thermal – Optical – Synthesis – Arc discharge – Laser Ablation.

#### Introduction

Iijima (1991) reported the observation of crystallizations and multiply layered tubular carbon nanostructures (MWCNT) in arc discharge soot in the early 1990s.

The synthesis of SWCNT was shortly demonstrated using a laser ablation technique. SWCNTS are visualized as seamlessly rolled-up sheets of graphenes and MWCNTS consist of co-axial concentric tubes of SWCNTS.

The molecular SWCNT is considered a new form of carbon, a sister material of  $C_{60}$  and distinct form of carbon allotropes such as graphite and diamond.

Nanotubes are ideal model for studying the physics & chemistry of 1D (one dimensional) solids, CNTs exhibit extraordinary properties such as high tensile strength and excellent electrical & thermal conductivities,

The electronics properties of SWCNT s behave as either metallic or semiconducting depending on their diameters and chiralities while MWCNTs depend on the features of each coaxial carbon shell and conduction takes place within the basal plane of graphite.

As synthesized SWCNT sample contain a mixture of metallic and semiconducting nanotube metallic SWCNTs are model system for studying rich quantum phenomena such as ballistic transport, single –electron charging, weak localization and quantum interference.

# **Carbon Nanotubes**

- A carbon Nano tube is a tube –shaped material made of carbon, having a diameter measuring on the nanometre scale.
- Carbon Nanotubes are formed from essential the graphite sheet & the graphite layer appear somewhat like a rolled-up continuous unbroken hexagonls mesh and carbon molecules at the apex of hexagon.
- ▶ Nanotubes are members of the fullerene structural family.
- Their name is derived from their long, hollow structure with the walls formed by one atom thick sheet of carbon called grapheme.

### **Types of carbon Nanotubes**

Classified mainly as

- Single walled Nanotubes
- Multi walled Nanotubes
- ➢ Torus

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# Single Walled Nanotubes

- Diameter: 1 nanometre
- ▶ Band gap: 0 2eV.
- > A one atom thick layer of grapheme into seamless cylinder
- > Their electrical conductivity can show metallic or semiconducting behaviour.
- SWNT can be formed in three different designs,
- Producing SWNTs
- Pass a carbon-containing gas like a hydrocarbon over a Nano-sized metal catalyst (Fe, Ni,or CO) Metal particles catalyse the breakdown of gaseous molecules into carbon.
- ▶ Nanotube begins to grow with the metal at one end.
- Poorer quality but better for volume production
- > Third method comes from vaporizing a metal graphite target with a laser
- Result in high yield of SWNTs

# (ii) Multi walled Nanotubes

- Multi-walled Nanotubes (MWNT) consist of multiple rolled layers (concentric tube of grapheme)
- $\blacktriangleright$  Interlayer distance : 3.4 A<sup>0</sup>
- > To describe structure of MWNT there are two models follow
  - 1. Russian doll model
  - 2. Parchment model
- More resistant to chemical change than SWNTs
- Producing MWNTS

The arc –evaporator apparatus produce the highest quality Nanotubes

The first Nanotubes had two layers with diameter ranging from 3 to 30 Nano meters pass 50 amps of current between two graphite electrodes in a cloud of helium.

Some of the graphite Vaporizes on the cathode containing carbon nanotubes

# Single Walled Nanotubes structure

The design depends on the way the grapheme is wrapped into a cylinder for example, image rolling a sheet of paper from its corner, which can be considered one design and a different design can be formed by rolling the paper from its edge.

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A SWNTS structure is represented by pair of indices (n,m) called chiral vector, the chiral vector is defined in the image below

Fig. 5.1 shows the basis vector  $a_1$  and  $a_2$  of the two dimensional unit cell of a graphite sheet, the axis vector T about which the sheet is rolled to generate the arm chair structure other orientations of T on the sheet generate the zigzag and chiral structures

The structural design has a direct effect on the nanotubes electrical properties, when n-m is a multiple of 3, then the nano tube is described as metallic (highly conducting) otherwise the nano tube is a semiconductor, the armchair design is always metallic while other design can make the nanotube a semiconductor.



Fig. 5.1 Basis vector for graphite sheet

#### Torus

It is a carbon nanotube bent in a torus shape. (i.e. doughnut shape)

#### Multi-Walled carbon nanotube structure

There are two structural models of MWNTs, In the Russian doll model, a carbon nanotube contains another nanotube inside it (the inner nanotube has smaller diameter than the outer nanotube).

In the parchment model, a single graphene sheet is rolled around itself multiple times resembling a rolled up scroll of paper. MWCNTs have similar properties to SWNTS yet the

outer walls on MWNTs can protect the inner carbon nanotubes from chemical interaction with outside materials. MWNTS also have a higher tensile strength than SWNTS.

#### **Electrical properties**

This structure of a carbon nanotube determines how conductive the nanotube is when the structure of atoms in a carbon nanotube minimizes the collision between conduction electrons & atoms, a carbon nanotube is highly conductive. The strong bonds between carbon atoms also allow carbon nanotubes to withstand higher electric currents than copper.

Electron transport occurs only along the axis of the tube. Single walled nanotubes can route electrical signals at speeds up to 10GHz. When used as inter connects on semi conducting devices nanotubes also have a constant resistivity.

#### Fabricatrion

#### Arc discharge method

A chamber containing a graphite cathode and anode contains evaporated carbon molecules in a buffer gas such as helium, the chamber also contains some amount of metal catalysed particles (such as cobalt nickel or iron). DC current is passed through the chamber, while the chamber is also pressurized and heated to ~4000K. In the course of this procedure, about half of the evaporated carbon solid difies on the cathode tip into a "cylindrical hard deposit" the remaining carbon condenses into "chamber soot" around the walls of the chamber and "cathode soot" on the cathode

The cathode soot and chamber soot yield either SW or MW carbon nanotubes. The cylindrical hard deposit doesn't yield anything particularly interesting.

The choice of buffer gas, the pressure of the chamber, and the metallic catalyst added to the chamber. Apparently the nanotubes grow from the surfaces of the metallic catalyst particles. These choices determine the shape and weather they are single or multi walled.

The advantage of this method is that it produces a large quantity of nanotubes. But the main disadvantage is that there is relatively little control over the alignment (i.e. chirality) of the produced nanotubes, which is critical to their characterization and role. Furthermore, due to the metallic catalyst included in the reaction, the produce need to be purified

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afterwards. Methods such as oxidation, centrifugation, filtration and acid treatment have been used and Fig. 5.2 shows the schematic diagram of arc discharge method.



Fig. 5.2 Arc discharge method for fabrication of carbon nanotubes

### Laser ablation Method

A quartz tube containing a block of graphite is heated in a furnace. A flow of argon gas is maintained throughout the reaction. A laser is used to vaporize the graphite with in the quartz. The carbon vaporizes, is carried away by the argon, and condenses downstream on the cooler wall of the quartz. This condensation is SWNT and metallic particles. Thereafter, purification methods are applied to this mixture.

The key to the proper formation of the condensed nanotubes is that the location where the carbon atoms begin to condense should be set up as a curved sheet of graphene with a catalyst metallic atom nearby. As carbon atoms begin to attach and form rings, the metallic atom, if it has the proper electronegativity properties, will preserve the open edge of the tube and prevent it from drawing to a close.

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Advantages of this technique include a relative high yield and relatively low metallic impurities, since the metallic atoms involved tend to evaporate from the end of the tube once it is closed.

Disadvantage: NTs produce from this method are not necessarily uniformly straight, but instead do contain some branching. Fig. 5.3 shows the experimental arrangement for the synthesis of carbon nanotubes by laser evaporation method.



Fig. 5.3 experimental arrangement for synthesizing carbon nanotubes by laser evaporation

### **Application of carbon Nanotubes**

The unusual properties of CNTs make possible many applications ranging from battery electrodes, to electronic devices, to re in forcing fibres, which make stronger composites,

For the application potential to be realized, methods for large-scale production of single-walled carbon nanotubes will have to be developed. The present synthesis methods provide only small yield and make the cost of the tubes about \$ 1500 per g.

On the other hand, large- scale production method based on chemical deposition have been developed for multi walled tubes.

### I. Field emission and shielding

When a small electric field is applied parallel to the axis of a nanotube, electrons are emitted at a very high rate from the ends of the tube, this is called field emission, this effect can be observed by applying a small voltage between two parallel metal electrodes, and spreading a composite paste of nanotubes on one electrode. A sufficient number of tube will be perpendicular to the electrode so that electron emission can be observed one application of this effect is the development of flat panel displays.

Television and computer monitors use a controlled electron gun to impinge electrons on the phosphors of the screen, which then emit light of the appropriate colors,

The high electrical conductivity of carbon nanotubes mean that they will be poor transmitter of electromagnetic energy.

A plastic composite of carbon nanotubes could provide lightweight shielding material for electromagnetic radiation this is a matter of much concern to the military, which is developing a highly digitized battle field for command, control and communication

### II. Computers

The feasibility of designing field-effect transistors (FETs), the switching components of Computers based on semiconducting carbon nanotubes connecting two gold electrodes has been demonstrated. An illustration of the device is shown in the fig. 5.4.



Fig. 5.4 A schematic diagram of a field-effect transistor made from a carbon nanotube.

When a small voltage is applied to the gate, the silicon substrate, current flows through the nanotube between the source and the drain.

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The device is switched on when current is flowing and off when it is not. It has been found that a small voltage applied to the gate can change the conductivity of the nanotube by a factor of  $>1X10^{6}$ , which is comparable to silicon field-effect transistors.it has estimated that the switching time of the devices will be very fast, allowing clock speeds of a terahertz which is  $10^{4}$  times faster than present processes.

The gold sources and drains are deposited by lithographic methods and the connecting nanotube wire is less than one nano meter in diameter this small size should allow more switches be packed on chip.

Another idea that is being pursued is to make a computer out of carbon nanotubes. The computer would be an array of parallel nanotubes on a substrate. Above this, but not touching the lower array and having a small separation which are carbon nanotubes oriented perpendicular to the tubes on the substrate. Each tube would be connected to a metal electrode. Fig. 5.5 illustrate the concept.



Fig.5.5 Illustration of the concept of a computer switching device mode from carbon nanotubes

The crossing points would represent the switches of the computer. When the tubes are not touching at the crossing point, the switch is off because the resistance is high.

In the ON state the tubes are in contact and have a low resistance, the ON and OFF configurations can be controlled by the flow of current in tube.

### III. Fuel cells

Carbon Nanotubes have application in better technology. Lithium, which is a

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Dr. B. Janarthanan Associate Professor Department of Physics Karpagam Academy of Higher Education Charger carrier in some batteries can be stored inside nanotubes. It is estimated that one lithium atom can be stored for every six carbon of the tube.

Storing hydrogen in nanotubes is another possible application, one that is related to the development of fuel cells are sources of electrical energy for future automobiles.

A fuel cell consists of two electrodes separated by a special electrolyte that allows hydrogen ions, but not electrons, to pass through it. Hydrogen is sent to the anode, where it is ionized. The freed electrons travel through an external circuit wire to the cathode. The hydrogen ions diffuse through the electrolyte to the cathode, where electrons, hydrogen, and oxygen combine to form water. The system needs a source of hydrogen. One possibility is to store the hydrogen inside carbon nanotubes, at present only about 4% hydrogen by weight has been successfully put inside the nanotubes. An elegant method e to put hydrogen into carbon nanotubes employs the electro chemical cell sketched in the fig. 5.6





The cell consists of an electrolytic solution of KOH with a negative electrode consisting of carbon nanotube (CNT) paper. Application of a voltage between the electrodes causes the  $H^+$  ion to be attracted to the

### **Thermal properties**

Graphite and diamond show extraordinary heat capacity and thermal conductivity. It can be expected that nanotubes have similar thermal properties at room and elevated temperatures because of the effect of phonon quantization. Both theory and experiment show that intertule coupling in SWNT bundles & MWNTs is weak in temperature region of > 100K.

Experimental result on MWNTs show a temperature dependent Specific heat, which is consistent with weak interlayer coupling, although different measurement show slightly different temperature dependencies.

When T>100K, an SWNT,SWNT bundle, and MWNT all follow or are close to specific heat relation of graphite about 700mJ/gK.However, at lower temperature ,CNTs show quantum confinement effects.

For example, the heat capacity (mJ/gK) is 0.3 for a (10,10) SWNT, no for SWNT bundle and graphite and 2 to 10 for a MWNT or bundle.

The thermal conductivity of both SWNTs and MWNTs should reflect the on-tube phonon structure regardless of inter tube coupling.

Measurements of the thermal conductivity of bulk sample show graphite like behaviour for MWNTs but quite different behaviour for SWNTs, specifically a linear temperature dependence at low T, which is consistent with one-dimensional phonons.

Thermal conductivity is one dimensional for nanotube like electrical conductivity. Therefore, the measurements give a broad range of 200 to 6000W/mK, again showing a strong dependence on the sample quality and alignment.

Theoretical calculation and experimental measurements showed that the thermal conductivity for a SWNT ropes and MWNTs at room temperature could vary between 1800 and 6000 W/mK. Whereas more than 3000 W/mK is firmly confirmed from the measurement of a single MWNT,

#### Hardness or Mechanical property:

 $\sigma$  Bonding is the strongest in nature and thus a nanotube that is structural with all  $\sigma$  bonding is regarded as the ultimate fibre with the strength in its tube axis,

Both experimental measurement and theoretical calculation agree that a nanotube is as stiff as or stiffer than diamond with the highest young's modulus and tensile strength.

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Table. 5.1 summarises calculated young's modulus (tube axis elastic constant) and tensile strength for (10,10) SWNT and bundle and MWNT with comparison with other materials. The calculation is in agreement with experiments on average.

Nano tube	Young's modulus	Tensile Strength	Density
	(GPa)	(GPa)	g/cm <sup>3</sup>
MWNT	1200	~150	2.6
SWNT	1054	75	1.3
SWNT bundle	563	~150	1.3
Graphite (in-plane)	350	2.5	2.6
Steel	208	0.4	7.8

Table. 5.1 Mechanical properties of nanotube

In general, various types of defect-free nanotubes are stronger than graphite. This is mainly because the axial component of  $\sigma$  bonding is greatly increased when a graphite sheet is rolled over to form a seamless cylindrical structure or a SWNT.

Young's modulus is independent of the tube chirality but dependent on tube diameter. The highest value is from tube diameter between 1 and 2nm, about 1TPa. Larger tube is approaching graphite and smaller one is less mechanically stable. When different diameter of SWNTs consists in a coaxial MWNT, the young's modulus will take the highest value of SWNT plus contributions from coaxial inter tube coupling or Vander waals force.

Thus, the young's modulus for MWNT is higher than a SWNT, typically 1.1 to 1.3TPa, as determined both experimentally and theoretically.

On the other hand, when many SWNTs are held together in bundle or a rope, the weak vanderwaal force induces a strong shearing among the packed SWNTs. This does not increase but decrease the young's modulus.

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The elastic response of a nanotube to deformation is also very remarkable. Most hard materials fail with a strain of 1% or less due to propagation of dislocations and defects. Both theory and experiment show that CNTs can sustain up to 15% tensile strain before fracture. Thus the tensile strength of individual nanotube can be as high as 150 GPa, assuming 1TPa for young's modulus, such a high strain is attributed to an elastic buckling through which high stress is release elastic buckling also exists in twisting and bending deformation of nanotubes.

All elastic deformation including tensile (stretching and compression), twisting ,and bending in a nanotube is nonlinear, featured by elastic buckling up to ~15% or even higher strain. This is another unique property of nanotube, and such a high elastic strain for several deformation modes is originated from  $Sp^2$  re hybridization in nanotubes through which the high strain gets released.

# **POSSIBLE QUESTIONS**

#### $\mathbf{UNIT} - \mathbf{V}$

1.Discuss mechanical and optical properties of carbon nanotubes.

2.Explain laser ablation method to synthesize carbon nanotubes.

3. What is carbon nanotubes? Explain types of carbon nanotubes.

4. Write a note on electrical and optical properties of carbon nanotubes.

5.Explain in detail how carbon nanotubes are synthesized by laser ablation.

6. What is nanotechnology? Write a short note on nanodevices.

7.Distinguish single walled and multi walled carbon nanotubes.

8.Explain how carbon nanotubes are synthesized by Arc discharge.

9. What is carbon nanotubes? Explain its type.

10.Discuss mechanical and thermal properties of carbon nanotubes.

# PART – C

1. What is carbon nanotubes? How it is synthesized using arc discharge and laser ablation.

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#### DEPARTMENT OF PHYSICS MSC PHYSICS (2017-2019) MATERIAL SCIENCE(17PHP105A) 2017-2018 (ODD) MULTIPLE CHOICE QUESTIONS

Unit V

Question	Option 1	Option 2	Option 3	Option 4	Answer
Who coined the word 'nanotechnology'?	Eric Drexler	Richard Feynmann	Sumio Tijima	Richard Smalley	Eric Drexler
The size of nanoparticles is between nm.	100 to 1000	0.1 to 10	1 to 100	0.01 to 1	1 to 100
"There is plenty of room at the bottom." This was stated by	Eric Drexler	Richard Feynmann	Harold Croto	Richard Smalley	Richard Feynmann
Who prepared and explained nanotubes for the first time?	Sumio Tijima	Richard Smalley	Eric Drexler	Richard Feynmann	Richard Smalley
Carbon atoms make type of bond with other carbon atoms.	covalent	ionic	metallic	hydrogen	covalent
Which of the following is an allotrope of carbon?	diamond	graphite	carbon nanotube	all of the above.	diamond
Fullerene or bucky ball is made up of carbon atoms.	100	20	75	60	60
There are types of CNT	2	3	4	1	2
Which of the following statement/s is are true?	Volume to surface area ratio is very large for nanomaterials.	The cut-off limit of human eye is 10-5 m.	Hardness of a SWNT is about 63 x 109 Pa.	Carbon nanotubes are cylindrical fullerenes.	Carbon nanotubes are cylindrical fullerenes.
The thermal stability of a nanotube is seen up toK in air.	100	1000	2000	3100	1000
The width of a carbon nanotube is nm	1	1.3	2.5	10	1.3
In radial direction, the thermal conductivity of a nanotube is watt/(m.K).	3500	385	350	0	0
The thermal stability of a nanotube is seen up to K in vacuum.	100	1000	2200	3100	3100
The thermal conductivity of an SWNT along length is watt/(m.K).	35	350	385	3500	3500
The tensile strength of an MWNT is Pa.	63 x 10 <sup>6</sup>	$63 \times 10^7$	63 x 10 <sup>8</sup>	63 x 10 <sup>9</sup>	63 x 10 <sup>9</sup>
The compressive strength of a nanotube its tensile strength.	is less than	is greater than	is equal to	may be greater than	is less than
The hardness of a standard SWNT is Pa.	63 x 10 <sup>6</sup>	$25 \times 10^6$	25 x 10 <sup>9</sup>	25 x 10 <sup>-9</sup>	25 x 10 <sup>9</sup>
The bulk modulus of a standard SWNT is that of diamond.	less than	greater than	equal to	less than or equal to	greater than
How much current can be passed through 1 cm <sup>2</sup> cross-section of a metal nanotube?	10 <sup>-9</sup> A	10 <sup>9</sup> A	1000 A	0.001 A	10 <sup>9</sup> A
The electrical conductivity of a nanotube is times that of copper.	10	100	1000	1/100	1000
An MWNT possesses electrical superconductivity up to temperature of	12 K	12°C	100 K	100°	12 K

The thermal conductivity of a standard SWNT along its length is watt/(m.K)	3500	385	35000	35	3500
Nanoscience can be studied with the help of	quantum mechanics	macro-dynamics	Newtonian mechanics	geophysics	quantum mechanics
Carbon nanotubes offer the advantage over metals of being:	good electrical conductors	light and flexible	good absorbers of heat	strong.	good electrical conductors
Nanotubes usually form in bundles. Which is the best description of such a bundle?	The tubes are connected together by covalent C-C bonds	The tubes are randomly organized, with the axes of the tubes lying in random directions	The tubes are aligned, axes parallel, with van der Waals forces operating between adjacent tubes	The bundles are of discrete sizes, and dipole- dipole forces hold the tubes together	The tubes are connected together by covalent C-C bonds
The structure of SWCNT can be conceptualized by wrapping athick layer of graphite into a seamless cylinder	ten atom	two atom	one atom	none of the above	one atom
A single-walled nanotube (SWNT) can have a diameter of and a length of	2nm,100µm	10nm,200µm	10mm,200µm	18nm,200mm	2nm,100µm
A single-walled nanotube (SWNT) can make a one dimensional structure called a	nanodot	nanoclusters	nanoparticles	nanowire	nanowire
Carbon nanotubes can be made by	laser evaporation	carbon arc methods	chemical vapor deposition	all the above	all the above
In laser evaporation method, a quartz tube containing argon gas and a graphite target are heated to	100°C	1200°C	1000°C	500°C	1200°C
In laser evaporation, thesweeps the carbon atoms from the high-temperature zone to the colder copper collector	oxygen	CO <sub>2</sub>	argon	hydrogen	argon
The Method can produce single-walled nanotubes of diameters 1-5nm with a length of 1µm	carbon arc method	laser evaporation	CVD	PVD	carbon arc method
Themethod allows continuous fabrication and the most favorable method for scaleup and production	chemical vapor deposition	laser evaporation	carbon arc	PVD	chemical vapor deposition
Most MWCNTs have a diameter of close to	100nm	10nm	1nm	1000nm	10nm
Inmethod a laser is aimed at a block of graphite	Laser ablation	Pulsed laser vaporization	CVD	both a and b	both a and b
In CVD, the synthesis of CNT is performed at At atm. Pressure	1100°C	500°C	100°C	3000°C	1100°C
method is used for the bulk production of SWCNTs	carbon arc method	laser evaporation	chemical vapor deposition	High-pressure CO conversion	High-pressure CO conversion
As the diameter of the nanotubes increases, the bandgap	decreases	increases	remains same	a or b	decreases
Magnetoresistance is a phenomenon whereby the resistance of a material is changed by the application of a	AC magnetic field	DC magnetic field	DC electric field	none of the above	DC magnetic field
The decrease in resistance with increasing DC magnetic field is	negative magnetoresistance	positive magnetoresistance	negative or positive magnetoresistance	none of the these	negative magnetoresistance
Carbon nanotubes have young's moduli ranging from	2.8-3.8TPa	1.28-1.8TPa	1.28-1.8Pa	1.28-1.8MPa	1.28-1.8TPa
Young's modulus of carbon nanotubes is almosttimes that of steel	10	20	100	2	10

Carbon nanotubes have soin their structure	many defects	few defects	moderate defects	all the above	few defects
The carbon-carbon bonds are	sp <sup>2</sup> hybrids	sp <sup>3</sup> hybrids	sp hybrids	sp <sup>2</sup> or sp hybrids	sp <sup>2</sup> hybrids
carbon nanotubes are abouttimes stronger than steel	30	10	20	2	20
Single electron tunneling occurs when the capacitance of the nanotube is	so small	high	moderate to low	very high	so small
In the metallic state the conductivity of the nanotubes is	very high	high	low	medium	very high
Carbon naotubes can carry aampheres per square centimeter	trillion	million	billion	thousand	billion
nanotubes have a very high thermal conductivity, almost a factor of more than that of	2, copper	4,diamond	2, silver	2, diamond	2, diamond
Advantages of carbon nanotubes on memory devices are	small diameter and low aspect ratio	low mechanical strength and aspect ratio	High aspect ratio and conductive along the axis	low conductivity and mechanical strength	High aspect ratio and conductive along the axis
Nano electronic devices using CNT can be manufactured using	Bottom up approach	top down approach	both a and b	none of the above	Bottom up approach
Advantages of carbon nanotubes based biosensors	high specificity and sensitivity	fast response	slow response	both a and b	both a and b
is a powerful technique to calculate how tubes of different dia. Are distorted when placed on a substrate	molecular mechanics	biosensors	memory devices	none of the above	molecular mechanics
The diameter of nanotubes used to form the rings is	3mm	1.4nm	5nm	100nm	1.4nm
The high Of CNTs means that they will be poor transmitters of electromagnetic energy	mechanical stability	thermal conductivity	electrical conductivity	none of these	electrical conductivity
CNTs are metallic or semiconducting, depending on the	diameter of the tube	chirality of the tube	temperature	both a and b	both a and b
There are a variety of structures of carbon nanotubes and these various structures haveproperties	same	different	both a and b	none of the above	different
In carbon arc, carbon atoms are ejected from theelectrode and form nanotubes on theelectrode	positive, negative	negative,positive	either a or b	none of these	positive, negative
If no catalysts are used, the tubes are	nested	multiwalled	single walled	either a or b	either a or b
The carbon arc method can produce	MWNT	nested	SWNT	all the above	SWNT

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		Reg. No				
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1 M.Se	I M.SC PHISICS, Iest - I					
MAI	ERIAL SCIE	NCE				
N	lax Marks: 50					
PART –	$A (20 \times 1 = 10)$	Marks)				
Answer <b>all</b> questions. Each ques	stion carries 1 n	nark.				
1. Thin film may be arbitrarily	defined as a sol	id layer having a thickness				
varying from a few Å to abo	ut					
a.10mm b.10cm	c.10µm	d.10^-3 nm				
2. Thickness of ultra thin film is	5					
a. >1000Å b. 50-100Å	c.100-1000Å	d. none of these				
3. An ideal film extended infini	tly in	directions but restricted				
along						
a. two and z direction	b. one and z d	irection				
c. three and none	d. none of these	se				
4. Highly conducting Na, K,Au	and Pt etc in th	e bulk form show -ve TCR				
when in thin film states thus bel	naving as					
a. semiconductors	b. conductors					
c. insulators	d. dielectrics					
5. A freshly formed film surface	e becomes high	ly reactive due to				
a. high volume to surface ratio	b. hig	h surface to volume ratio				
c. high thickness	d. none of the	se				
6. Characteristic of a surface are	e more often ob	served in				
a. amorphous b. sing	e crystal	c. polycrystalline				
d. thin films						
7. Thin films can be prepared fr	om a varietv of	materials such as				
a. metals b.Semiconductors	c. insulato	rs d. all the above				
8. The primary requirement for	the methods (a)	) Thermal deposition and				
Sputtering is a						
a high vacuum b high	er than ambient	pressure				
c ambient pressure d none	of these	prossure				
9 involves the evapor	ation or sublim	nation of the material in vacuo				
by thermal energy						
a Sputtering b CVE	) c The	rmal deposition				
d chemical deposition	<i>c.</i> 1110					
10 When all the molecules are	condensed stic	king coefficient has a may				
value of	condensed, stie	the coefficient has a max.				
a 100 b 1	c 10	d 1000				
11. In electron diffraction tec	hnique maxim	num voltage upto				

b. 60-65eV a. 60-63keV c. 60-65keV d. 60-63eV 12. .....Is used to analyse the surface layers of metals, semiconductor and insulators a. SEM b. LEED c. XPS d. HEED 13. The surface layers of Ni single crystal was first made by..... b. Thomson c. germer d.both a and b a. Davisson 14. In Finch type camera, a maximum voltage is limited upto ..... a. 100keV b. 200keV c. 65keV d. 40keV 15. In HEED method the accelerating potential of electrons is about ..... b. 60 to 200keV a. 40 to 100keV c.5 to 500eV d. both a and b 16. In LEED method the accelerating potential of electrons is about ...... a. 5 to 500eV b. 60 to 200keV c.40 to 100keV d. none of these 17. For transmission method the material thickness should be lower than . . . . . . . . c. 10000Å d. 13000Å a. 1000Å b. 500Å 18. The vacuum conditions in LEED is in an order of ..... a. 10^-9 to 10^-10 torr b. 10<sup>-4</sup> to 10<sup>-6</sup> torr c.10^-1 to 10^-2 torr d. < 10^-1 torr 19. .....is used as a standard material in HEED b.magnesium c.copper a.graphite d.tin 20. Which method provide information of both surface layers and different layers constituting the material can be d. TEM a. LEED b. HEED c.SEM

#### PART – B

Answer the questions 21. What are the deposition techniques available for developing thin films?

- 22. Distinguish between electron beam method and cathodic sputtering.
- 23. What is meant by chemical deposition?

Answer the questions

PART - C

#### $3 \times 8 = 24$

 $3 \ge 2 = 6$ 

24. a. Write a note of distribution of deposits.

#### OR

- b. Explain about the thermal evaporation for the deposition of thin films.
- 25. a. Explain the mass method for the determination of thickness of the film. OR

b.Briefly explain the electron beam method for deposition of thin films 26. a. Elaborate about the high energy electron diffraction technique.

#### OR

b.Explain the low energy electron diffraction technique.

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#### I Internal Answer key

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Max Marks: 50

PART – A (20 × 1 = 10 Marks)

Answer all questions. Each question carries 1 mark. 1. Thin film may be arbitrarily defined as a solid layer having a thickness varying from a few Å to about a.10mm b.10cm c.10µm d.10^-3 nm 2. Thickness of ultra thin film is a. >1000Å b. 50-100Å c.100-1000Å d. none of these 3. An ideal film extended infinitly in ..... directions but restricted along..... b. one and z direction c. three and none a. two and z direction d. none of these 4. Highly conducting Na, K,Au and Pt etc in the bulk form show -ve TCR when in thin film states thus behaving as a. semiconductors b. conductors c. insulators d. dielectrics 5. A freshly formed film surface becomes highly reactive due to a. high volume to surface ratio b. high surface to volume ratio c. high thickness d. none of these 6. Characteristic of a surface are more often observed in ..... d. thin films b. single crystal a. amorphous c. polycrystalline 7. Thin films can be prepared from a variety of materials such as b.Semiconductors c. insulators a. metals d. all the above 8. The primary requirement for the methods (a) Thermal deposition and Sputtering is a a. high vacuum b. higher than ambient pressure c. ambient pressure d. none of these 9. .....involves the evaporation or sublimation of the material in vacuo by thermal energy a. Sputtering b. CVD c. Thermal deposition d. chemical deposition 10. When all the molecules are condensed, sticking coefficient has a max. value of ..... a.100 **b**. 1 c. 10 d. 1000 11. In electron diffraction technique maximum voltage upto ..... c. 60-65keV d. 60-63eV a. 60-63keV b. 60-65eV 12. .....Is used to analyse the surface layers of metals, semiconductor and insulators b. LEED c. XPS d. HEED a. SEM 13. The surface layers of Ni single crystal was first made by..... a. Davisson b. Thomson c. germer d.both a and b 14. In Finch type camera, a maximum voltage is limited upto ..... d. 40keV b. 200keV c. 65keV a. 100keV 15. In HEED method the accelerating potential of electrons is about ..... b. 60 to 200keV c.5 to 500eV d. both a and b a. 40 to 100keV 16. In LEED method the accelerating potential of electrons is about ..... b. 60 to 200keV a. 5 to 500eV c.40 to 100keV d. none of these 17. For transmission method the material thickness should be lower than ..... a. 1000Å b. 500Å c. 10000Å d. 13000Å 18. The vacuum conditions in LEED is in an order of .....

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a. 10^-9 to 1	10^-10 torr	b. 10^-4 to 2	10^-6 torr	c.10^-1 to 10^-2 torr	d. < 10^-1 torr
19is u	ised as a standard	material in HI	EED		
a.graphite	b.magnesium	c.copper	d.tin		
20. Which me	ethod provide info	rmation of bo	th surface	layers and different layers	constituting the material
can be					
a. LEED	b. HEED	c.SEM	d. TEN	N	
			PART	– <b>B</b>	

#### Answer the questions

 $3 \ge 2 = 6$ 

#### 21. What are the deposition techniques available for developing thin films?

The deposition techniques for developing thin film is Electron Beam Method, Cathodic

Sputtering, Glow Discharge Sputtering, Chemical Vapor Deposition or Vapor Plating and Electro Deposition

#### 22. Distinguish between electron beam method and cathodic sputtering.

#### Electron Beam Method

This is one of the best method for the deposit of metals, alloys refractory metal etc., as high rate and is now routinely used for the production of the metal film resistor and others.

Multi-electron beam source are also used for special applications.

In this technique an electron beam accelerator with a voltage of say 2 - 10kv is focused on the surface of charge which is normally kept inside a graphite crucible placed on a water cooled upper block (Copper block).

The high energy electron beam emitting form the cathode impinge on the charge as the same potentials the anode converted into intense heat energy which melts the charge.

### Cathodic Sputtering

The deposition of metal films by sputtering from a cathode by the glow discharge method was first observed by grove.

The sputtering phenomena is the ejection of atoms from the cathode surface by impinging of energetic positive ions of noble gases such as helium, Ar, Ne, Kr at a reduced pressure under a high dc voltage. By this technique, it is possible to make various resistive, semiconducting, superconducting and magnetic films.

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I Internal Answer key

23. What is meant by chemical deposition? Chemical deposition

This method depends on the deposition of films from aqueous solution either by passing a current or by chemical reaction under appropriate conditions and is generally used for the deposition of thick metallic or alloy films. By the nature of their preparation conditions film are not generally of high purity.

Despite this limitation this technique is widely used for the fabrication of conducting connectors, magnetic memory elements.

With an appropriate control the deposition parameter such as bath composition, temperature, pH, current density etc. metallic deposits and even alloys of definite composition can be obtained.

 $3 \ge 8 = 24$ 

#### PART – C Answer the questions 24. a. Write a note of distribution of deposits. Distribution of deposit

Evaporate molecules issuing out from heated sources will spread out in all directions but their velocity distributions will depend on the nature of the source which can be broadly classified as (i) point source (ii) surface source (iii) cylindrical source.

(i)If a source can be approximated to a tiny sphere compared to its distance from the receiving substrate, then the emitted vapor stream will have the same velocity distribution in all direction thus resembling the emission from a point source such a type of source is known as the point source.

For (ii), the emission velocity of the vapor stream will be directional and maximum along the source normal direction but it will decrease with increase of the angle of inclination ( $\psi$ ) of the direction with the source normal. The velocity distribution will follow the cosine law and decrease with increase of  $\psi$  such a source is called a directed surface source. If  $\psi=0$ , then a surface source resembles a point source except that it is not spherical in the category (iii), the emission of vapor stream will be from the surface of a cylinder and can be approximately between an idealized point source and a surface source.

# **MATERIAL SCIENCE (17PHP105A)**

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# I Internal Answer key

There are several types of practical heating sources made from refractory metals such as tungsten, molybdenum, tantalum etc. and their emission characteristics can be approximated to one of the above three categories.

There source may be made from single or multi stranded filaments to various shapes or from straight strips with or without any dimple at the centre or in the form of a boat and sometimes having the shape of a cylinder etc.(Fig. a,b,c,d).



Fig 1. Evaporation source of different types:

a-hair pin type, b- wire helix, c- wire basket, d- dimple foil, e-dimple foil with refractory oxide coating, f- canoe type.

The amount of deposits received by a substrate will depend not only on the nature of the source but also on the inclination of the vapor stream ( $\theta$ ) with the substrate normal direction. Let us now consider the amount of material (dm), that will be emitted through a solid angle d $\omega$  of a source which may be in the form of a point or surface source. If m is the total amount of the material evaporated, then for the case (i), i.e point source

$$dm = \frac{m}{4\pi} d\omega \tag{1}$$

Case (ii) i.e surface source

$$dm = \frac{m}{\pi} \cos\varphi d\omega \tag{2}$$

If dA is the unit area of the substrate at a distance r from the source along the vapor direction (Fig.2) then the amount of material deposited on to the substrate will also depend on  $\theta$  and the expression (1) and (2) then take the forms.

(i) for point source

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$dm = \frac{m}{4\pi r^2} dA$ , when $\theta = 0$		(3a)
$dm = \frac{m}{4\pi r^2} \cdot cos\theta dA$ , when $\theta \neq 0$		(3b)
(ii) for a source surface		
$dm = \frac{m}{\pi r^2} \cdot \cos\psi dA$ , when $\theta = 0$		(4a)
$dm = \frac{m}{\pi r^2} \cdot cos\psi cos\theta dA$ , when $\theta \neq$	60	(4b)
	0	



Fig.2 A general configuration of the evaporation source o and the substrate A,  $\psi \& \theta$  are the angles subtended by the normal to the vapor source and substrate surface respectively to vapor direction, d $\omega$  being the solid angle through which the mass evaporates and r is the distance between the vapor source and the substrate, dA being the unit area of the substrate.

The above relation means that the substrate will receive a maximum amount of deposits when  $\theta$  or  $\psi$  or both will be zero. Hence the positioning of the substrate with respect to the source as well as the nature of the source considerably affects the film thickness. If  $\rho$  is the density of the material evaporated and t is the thickness, then Eqs. (3a-4b) can be replaced respectively by the following expressions,

For (i) when  $\theta=0$ 

(5a)

When  $\theta \neq 0$ 

$$t = \frac{m}{4\pi\rho r^2}\cos\theta \tag{5b}$$

For (ii) when  $\theta=0$ 

$$t = \frac{m}{4\pi\rho r^2}\cos\psi \tag{6a}$$

When  $\theta \neq 0$ 

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**2017-2018 (Odd)**  $t = \frac{m}{4\pi\rho r^2} \cos \psi \cos \theta$ 

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(6b)

Let us now consider the thickness variation of the deposits at different points on the horizontal plane PQRS which is at a distance h from the source. If x is the distance of any point under consideration from the position where the source normal meets plane (Fig. 3) and if the film thickness at two points A & B be to & t, respectively, then for a point source we have



Fig. 3 configuration illustrates any arbitrary position (B) and the source normal position (A) lying in a horizontal plane of a substrate (PQRS) separated by a distance (X); h & r the distance of A & B from the source O,  $\psi$  being angle subtended by the normal to the vapor source O to the vapour direction OB.

t<sub>o</sub>=
$$\frac{m}{4\pi\rho}$$
.1/h<sup>2</sup> → (7a)  
t<sub>1</sub>= $\frac{m}{4\pi\rho h^2 \left[1 + \left(\frac{x}{h}\right)^2\right]^{3/2}}$  → (7b)  
t<sub>1</sub>/t<sub>0=</sub>  $\left[1 + \left(\frac{x}{h}\right)^2\right]^{3/2}$ 

where  $\cos\theta = h/r$  and  $r^2 = h^2 + x^2 \rightarrow (8a)$ 

for a surface, we have

$$t_0 = \frac{m}{\pi \rho} \cdot \frac{1}{h^2}$$
,  $t_1 = \frac{mh^2}{\pi \rho (h^2 + x^2)^2} \rightarrow (8b)$ 

$$mh2/\pi\rho h4(1+\frac{x^2}{h^2})2 = mh2/\pi\rho h2(1+\frac{x^2}{h^2})2$$

Dr. B. Janarthanan Associate Professor Department of Physics Karpagam Academy of Higher Education **I Internal Answer key**  $t_1/t_{0=} \left[ 1 + \left(\frac{x}{h}\right) 2 \right] - 2$ 

Where  $\cos\theta = \cos\psi = h/r$ .

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In the thermal deposition method, vacuum and should be as high as possible i.e the residual vapour pressure should be very low and preferably below 10<sup>-5</sup> torr or even lower. The evaporate stream of molecules will then have a large mean path and strike the substrate without any significant loss of their kinetic energy due to the collisions of residual gas molecules.

The residual but very low pressure in the vacuum chamber also ensures the non formation of any oxide layer during the evaporation of metals and alloys. If the vacuum is poor i.e when the residual air pressure is not low, then the deposits are likely to be contaminated with some oxides formed during the deposition process and often become blackish and powered and non adherent to the substrate.

A high substrate temperature generally improves the physical characteristics of the deposited films by importing greater mobility to the vapor molecules or atoms condensing over the substrate for migration over the surface.

Uniformity of the deposit thickness over the substrate surface is generally achieved by placing the substrate at an appropriate distance from the evaporant source and also rotating it either around its axis or that of the source or both as the case may be.

### **b.Explain about the thermal evaporation for the deposition of thin films.** *Thermal evaporation*

Refractory metals like tungsten, molybdenum or tantalum are generally used in the form of wire or strip having different shapes. The choice of particular refractor metal as a heating source depends on the material to be evaporated so that the evaporant material does not react with the refractory metal at the high temperature of evaporation however, the formation of alloy with the source cannot always be avoided. Hence a coating of refractory oxides such as Al<sub>2</sub>O<sub>3</sub>, BeO or other suitable materials is often given over the filament or strip so as to prevent a direct contact between the molten charge and the refractory metal. In any case, when a direct heating of the charge is made, the filament or strip is precleaned by passing a heavy current through it so as fox a binary alloy partial pressure of the constituent component may be assumed to follow Raouts law for dilute solutions i.e the vapor pressure of each component is depressed compare to that of the

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pure state by an amount proportional to its concentration. Equation denoting the rate of evaporation of pure element may also be extended to the binary alloys.

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Thus for two pure elements A and B the rates of evaporation at a temperature T and with partial vapour pressures  $P_A$  and  $P_B$  may be denoted as  $E_A$  and  $E_B$  respectively.

If MA and MB are the molecules weights of A and B, then the ratio of the rates deposition of the two will be

$$\frac{EA}{EB} = \left[\frac{PA}{PB}\right] \left[\frac{MA}{MB}\right]^{1/2} \tag{9a}$$

Assuming that Raoult's law of depression of vapor pressure is valid for the binary alloy system A B, then according to Holland , the ratio of evaporation of two components A and B from the alloy, will be

$$\frac{EA}{EB} = \frac{WA}{WB} \cdot \left[\frac{PA}{PB} \frac{\sqrt{MB}}{MA}\right]$$
(9b)

Where  $W_A$  and  $W_B$  are the weight concentration S of the two components A and B in the binary alloy AB. If it is assumed that the sticking coefficient of the two components are the same ,then  $E_A/E_B$  ratio will also represent the deposit composition of the alloy on the substrate. It is thus seen that the composition depends not only on the initial alloy composition but also on the factor the parenthesis in eq 1b and less the later is unity which is not usually so , the deposit composition will not fallow the bulk alloy composition i.e  $W_A, W_B$ . A typical case of the variation of deposit composition is a alloy, say of composition 80: 20 Nickel and Chromium. A continuous vacuum evaporation of the above metals leads to film initially of composition 70:30 and later 50 : 50 to make it white hot for a very short period so that all the surface impurities to the filament or the strip are removed by evaporation and the process is called flash cleaning.

After the above cleaning of the filament, strip or boat whatever may be the form of the evaporating source a little amount the charge is then put into it and a current is slowly passed through the source and gradually increased so that the melt forms a layer over the heating source. Usually a shutter is placed in between the heating source and the substrate so that no vapor stream of the charge can reach the substrate.

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When appropriate deposition conditions are established, ie, vacuum filament and substrate temperature, source to substrate distance inclination etc... the shutter is then removed out of the line of vapor stream of the charge in vacuum and the substrate starts,

In the required film thickness is obtained. This is again brought into the original position in vacuum so as to put of further deposition on the substrate and the heating of the filament is then gradually stopped.

In the charge consist of two or more constituents which have different vapor pressures, then the one having higher vapor pressure will tent to vaporize at lower temperate than the other. This happens in any alloy systems. This means the composition of the vapor stream of the charger will different from that of the charge itself. And when condensed the deposit will have different deposition even assuming the condensation rate is the same for all the constituent species further in addition to the vapor pressure that the evaporation rate of species depends on its molecular weight, temperature

# **25. a. Explain the mass method for the determination of thickness of the film.** *Mass Methods: Microbalance Technique*

This methods depends on the increase of the weight of a film due to its mass increase and from the knowledge of its density and the deposited area, film thickness (d or t) can be evaluated from the relation.

d or t = $W/\rho A$ 



Fig.1(a) quartz fiber type microbalance

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Solenard 131	Torsion fibor
magnet	
nomen.	7/ Thise-odge
A	A
	Spring callbration pan
	valve.

Fig.1(b) torsion fiber suspension and electromagnetic force compensation type balance Where W is the weight difference of the film,  $\rho$  density and A is the deposited area. The increase in the film weight can be measured by a suitable micro balance. The above technique with appropriate modifications as in a quartz fiber microbalance can be used as a rate monitoring system also.

This balance is mode of quartz and the deposits are formed on a pan which is suspected from the end of a beam by means of a quartz fibre, the other end carrying a counter poise. A pointer or a mirror is attached to the beam of the balance.

With the increase of weight of the film the pointer moves and its displacement with reference to a fixed point can be measured with a telescope and in the case of a mirror by means of a lamp and scale arrangement. The movement of the pointer can be standardized against known weights.

Alternatively, the balance can be modified in such a way that the deflected beam can be brought back to its original position by a suitable magnet and a solenoid coil through which an appropriate current is passed, the change in current being proportional to the increase in the weight of the deposit.

In other variation of the technique a quartz spring with a pan attached to it is used. An increase in weight of the film will extend the spring and the elongation will be proportional to the mass deposited.

This system can be used both as a thickness meter as well as a monitoring system. The sensitive of a microbalance is the order of  $10^{-7}$  to  $10^{-8}$  g and can be improved further.

# M.Sc PHYSICSMATERIAL2017-2018 (Odd)I Internal Answer keyb. Briefly explain the electron beam method for deposition of thin filmsElectron Beam Method

This is one of the best method for the deposit of metals, alloys refractory metal etc., as high rate and is now routinely used for the production of the metal film resistor and others.

Multi-electron beam source are also used for special applications.

In this technique an electron beam accelerator with a voltage of say 2 - 10kv is focused on the surface of charge which is normally kept inside a graphite crucible placed on a water cooled upper block (Copper block).

The high energy electron beam emitting form the cathode impinge on the charge as the same potentials the anode converted into intense heat energy which melts the charge.

By suitably focusing the electron beam and controlling its intensity it is possible to heat the top surface of the charge in a mountain condition from which evaporation can take place. As a result a fresh surface id=s exposed every time for further melting and evaporation.

Hence a deposit of more or less of a constant composition is obtained. The temperature attained by the charger at the surface can be as high as above  $3000^{\circ}$ C or by this method and hence refractory metals such as W, Mo, Ta etc can be melted and evaporated by this technique.

There are three types of electron beam guns (Fig. 4)

- A. Work accelerated gun where electron beam coming out of a loop type of a filament. It is accelerated directly towards the charge or through an appropriate shield thus concentrating the beam
- B. Self accelerated gun where the electrons are emitted from hair pin type of filament and focused through a Wehnelt cylinder on the material.
- C. Bent beam electron gun, where a beam of electrons is bent by an appropriate magnetic field, and then focused on the charge.

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Electron Beam method

# **26. a. Elaborate about the high energy electron diffraction technique.** *High Energy Electron Diffraction (HEEDd)*

Monochromatic electrons are emitted from a hot or cold cathode under an accelerating field of high voltage say between 60 to 200 keV and pass through an aperture on a diaphragm which works as the anode normally at the earth potential. The body of the instruments is also connected to the earth.

The negatively accelerated electrons beam generated under a highly stabilized power source. Than passes through a magnetic or electrostatic lens for containing the beam and then sickness the specimen surface either at a low glancing incidence or is transmitted through it.

By controlling the lens current both the central and diffracted electron beams can be focused on a florescent screen.

A high vacuum pumping system is used to evaluate the high equipment to about  $10^{-4}$  to  $10^{-6}$  torq.

The design of the specimen holder is such that it can be rotated along an axis moved forward and backward and even titled so as to facility point to point investigation of specimen films by reflection or transmission method.

A diffraction pattern from a single crystal from a to the reciprocal lattice net word of real crystal lattice magnified lambda L times when recorded on a plate or observed on a screen lambda and L is the distance between the monochromatic beam and L is the distance between the specimen and the photographic plate. In the photographic plate, the spot obtained correspond to

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different planes of the crystal which fulfil the Bragg reflection condition, constitute with the electron beam diffraction and can be identified from their geometrical disposition and also by measuring  $d_{hkl}$  of each spot provided  $\lambda l$  and lattice parameter are known since the surface of a sphere of reflection for high energy electrons. Hence by indexing and identifying these reciprocal lattice spots crystal lattice spacing can be evaluated from the relation.

 $\lambda L = r1d1 = r2d2 = r3d3....etc$ 

where  $\lambda$  is the wavelength of the monochromatic electron beam and L is the distance between the specimen and the screen r1, r2, r3.... Are respectively the spot distance from the undeflected beam spot and d1,d2,d3....etc are the interplanar spacing of different spacing of the different planes of specimen under investigation for an accurate determination of  $\lambda$ L which depends on the electron energy. A standard material yielding sharp diffraction spots or rings is used under investigation and diffraction pattern from both of them are simultaneously recorded on the plate. Generally (11230) reflection of graph plate (d = 1.230A<sup>0</sup>) is used as a standard.

The accelerating potential of electrons is about 40-100kev or even more specimens can examined by reflection method and when thin also by transmission technique.

### **b. Explain the low energy electron diffraction technique.** *Low Energy Electron Diffraction (LEED)*

The use of low energy electrons (5-500eV) for studying the surface layers if nickel singe crystal was first made by Davison and Germer.

Slow electrons because of their low energy interact strongly with matter and are completely scattered by the surface atoms. Since the scattering of electrons is also elastic, the surface layer atoms behave as 2D rather than 3D scatterers. The depth of penetration of slow electrons is about a few  $A^0$  compared to about 10-20  $A^0$  for the HEEP.

The diffraction is similar in both case except that the elastically back scattering electrons are utilised for observing the diffraction pattern rather than the transmitted once as in sum HEED cases. Further the vacuum conditions in LEED is much more stringent and an order of  $10^{-9}$ -10— $^{10}$ torq. Is essential for studying the surface layers

The instrument in it basic design consist of an electron emitting source (V shaped W filament) having negative accelerating voltage of about 5-500 eV (1), a Weinent cylinder (2) and it is followed by a lens systems (3). Electrons after passing through the above strike the crystal

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surface (4) & the back scattering electron than pass through grids (5,5'). The space between the crystal and the first grid (5) is generally field free, so that the diffracted electrons can go straight lines. The second grid (5<sup>1</sup>) knows as repel is approximately at the same potential as the cathode , so that the in elastically scattered electrons cannot pass through the grid to the florescent screen (6), which is kept at a high positive potential say ...

The diffracted electrons after passing through the repelling grid are further accelerated by the high potential of the florescent screen where the diffraction pattern is observed and it can be recorded.

The whole system is evacuated by a high vacuum pump system (7) comprising of a high capacity sorption pump, a getter pump, etc., the crystal (4) can be suitably manipulated to provide rotations, to and few movements or tilt etc. so that the different areas of the crystal surface can be exposed to the impinging slow electrons.

A LEED study concurs primarily about the nature of the surface layer consisting of a few atomic plans, surface contamination, formation of oxide layers, nature of clean surface, etc. since the study involves a change in the surface in the presence of a minute amount of gas or due to adsorption or reactions or reactions in high vacuum the diffraction patterns from the new surface layers thus formed are referred with respect to the initial clean surface.

#### Reg. No..... [17PHP105A]

KARPAGAM ACADEMY OF HIGHER EDUCATION **COIMBATORE -641 201** I M.Sc PHYSICS **II Internal Examination** MATERIAL SCIENCE

Max Marks: 50

#### $PART - A (20 \times 1 = 10 Marks)$

Answer **all** questions. Each question carries 1 mark. 1. In Bridgman technique, the rates of movement are mostly in the range..... a. 1-30mm/hr b. 0.1-200mm/hr d. above 300mm/hr c. 200-300mm/hr 2. The advantages of the Bridgman technique are..... a. low-cost b. suitable for low melting point materials c. adhesion of the solid materials to the ampoule wall d. both a and b 3. In Bridgman technique, the melt temperature ...... With distance from the solid-liquid interface a. decreases b. increases c. increases or decreases d. constant 4. A disadvantage in Bridgman technique is..... a. nucleate dislocations in the material b.low-cost c. adhesion of the solid materials to thee ampoule wall d. both a and c 5. The container wall acts as a preferential, spurious nucleation site, resulting in..... a. polycrystalline growth b. single crystal growth c. amorphous growth d. single or polycrystal growth 6. The requirement that the freezing isotherm should move systematically through the molten charge can be satisfied by moving a. the crucible b. the furnace c. changing the furnace temperature d. any one of the above 7. The Bridgman technique cannot be used for materials which..... a. decompose before melting b. undergo solid state phase transformation c. decompose after melting d. both a and b 8. Bridgman technique is best suited for..... a. high melting point materials b. high vapour pressure materials c. low melting point materials d. both high and low melting point materials 9. The characteristic of a container..... b.smaller coefficient of thermal expansion a. not react with the melt c.smaller thermal conductivity than the crystal than the crystal

d. all the above

10. The materials with covalently bound crystals are often compatible with containers made of ..... d. platinum a. glasses b. gold c. silver 11. Who coined the word 'nanotechnology'? a. Eric Drexler b. Richard Feynmann c. Sumio Tijima d. Richard Smalley 12. The size of nanoparticles is between \_\_\_\_\_ nm. a. 100 to 1000 c. 1 to 100 b. 0.1 to 10 d. 0.01 to 1 13. "There is plenty of room at the bottom." This was stated by b. Richard Feynmann c. Harold Croto a. Eric Drexler d. Richard Smallev 14. Who prepared and explained nanotubes for the first time? a. Sumio Tijima b. Richard Smalley c. Eric Drexler d. Richard Feynmann 15. Carbon atoms make \_\_\_\_\_ type of bond with other carbon atoms. d. hydrogen a. covalent b.ionic c. c. metallic 16. Which of the following is an allotrope of carbon? c. carbon nanotube b. graphite a. diamond d. all of the above. 17. Fullerene or bucky ball is made up of carbon atoms. b. 20 a. 100 c. 75 d. 60 18. There are..... types of CNT b. 3 a. 2 c. 4 d.1 19. Which of the following statement/s is are true? a. Volume to surface area ratio is very large for nanomaterials. b. The cut-off limit of human eye is 10-5 m. c. Hardness of a SWNT is about 63 x 109 Pa. d. Carbon nanotubes are cylindrical fullerenes. 20. The thermal stability of a nanotube is seen up to K in air. a. 100 b. 1000 c.2000 d. 3100

### Part – B

### Answer all the Ouestions

21. State Bragg's law

- 22. What is the importance of single crystal.
- 23. Give the techniques for growing crystals

### Part – C

### Answer all the Questions

 $(3 \times 8 = 24)$ 

 $(3 \times 2 = 6)$ 

24. a. Briefly explain the melt growth of oxide crystals for saw, piezoelectric and nonlinear optical applications

- b. Explain the working of heat exchanger method with neat sketch
- 25. a. Discuss mechanical and optical properties of carbon nanotubes OR
  - b. Explain laser ablation method to synthesize carbon nanotubes
- 26. a. Explain Periodic bond chain theory
  - OR
  - b. Explain crystal pulling technique