<u>UNIT-I</u>

SYLLABUS

SEMESTER – II

THIN FILM PHYSICS

17PHP205C

L T P C 4

- - 4

Scope: Due to the large surface to volume ratio, thin films behave differently compared to bulk materials, which make them useful in many applications like solar cell, sensors etc. Objectives: To give idea to the students about the different aspects of thin films, their preparation methods, characterizations, applications etc.

UNIT – I

Preparation of Thin Films:Spray pyrolytic process – characteristic feature of the spray pyrolytic process – ion plating – Vacuum evaporation – Evaporation theory – The construction and use of vapour sources – sputtering Methods of sputtering – Reactive sputtering – RF sputtering - DC planar magnetron sputtering



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KARPAGAM ACADEMY OF HIGHER EDUCATION (Deemed to be University Established Under Section 3 of UGC Act 1956) Coimbatore – 641 021.

LECTURE PLAN DEPARTMENT OF PHYSICS

STAFF NAME: Dr.E.SIVA SENTHIL SUBJECT NAME: THIN FILM PHYSICS SEMESTER: II

SUB.CODE:17PHP205 CLASS: I M.Sc(PHY)

S.No	Lecture	cture Topics to be Covered	
	Duration		Material/Page
	Period	LINET 1	Nos
		UNIT-I	
1.	1	Introduction to Thin Film	T1:5-6
2.	1	Preparation of Thin Film	T1:5-6
3.	1	Spray pyrolytic process	T1:5-6
4.	1	characteristic feature of the spray pyrolytic process	T1:5-7
5.	1	ion plating	T1:5-8
6.	1	Vacuum evaporation	T1:1-7
7.	1	Evaporation theory	T1:1-26
8.	1	Introduction to Vapour Sources	T1:5-6
9.	1	The construction and use of vapour sources	T1:3-9
10.	1	Continuation	T1:3-9
11.	1	sputtering Methods of sputtering	T1:7-50
12.	1	Reactive sputtering	T1:4-26
13.	1	RF sputtering	T1:4-31
14.	1	DC planar magnetron sputtering.	T1:4-33
15.		Revision	
	Total No of H	Iours Planned For Unit 1=15	

TEXT BOOK:

1. Meissel. L.T and R. Glang., 2000, Hand book of thin film technology, Tata McGraw Hill, New Delhi.

REFERENCE:

 Anderson, J.C.2011 Ist edition The use of thin films in physical investigation, Academic press
 Berry, Hall and Harris.2003, illustrated edition Thin films technology, Van Nostrand Reinhold publishing

3. Chopra, K.L. Ist edition 2004, Thin film Phenomena, Mc Graw hill

4. Chopra, K.L. and Das, S.R Ist edition2013 Thin films solar cells.springer

Unit I

<u>Spray pyrolysis</u>

It is a **process** in which a thin film is deposited by **spraying** a solution on a heated surface, where the constituents react to form a chemical compound. The chemical reactants are selected such that the products other than the desired compound are volatile at the temperature of deposition.

Principle:

Spray pyrolysis involves a thermally stimulated chemical reaction between constituent ions to form the required compound. In this technique, a solution containing the soluble salts of the constituent atoms of the required compound is sprayed on to a hot substrate in the form of fine droplets, using a sprayer. Usually compressed air will be the carrier gas. But compressed nitrogen is also used as carrier gas to avoid the presence of oxygen. The sprayed droplets reaching the hot substrate surface undergo pyrolytic decomposition and form the compound as a thin film on the surface of the hot substrate. In fact it is the hot substrate which provides the thermal energy needed for the decomposition and subsequent recombination of the constituent species. The other volatile by-products and the excess solvents are converted into vapourphase and are removed-from the site of chemical reaction by using an exhaust fan. Carrier gas here plays an active role in the pyrolytic reaction process especially in the case of oxide films. Doping can be easily accomplished by simply dissolving the dopants in the required quantity in the spray solution. Only thing to be noted here is that the soluble salt of the dopant should be available. Such an attempt is made in the present work in order to prepare indium doped cadmium supplied films. Here characterization of the film is required for knowing the quantity of dopant available in the film. Actually in

Our work, we varied the concentration of the dopant and the characterization of the films was also done. Even multi component doping can be done on different layers of the film, using this technique.

Characteristic features of the spray pyrolysis process:

The growth rate of the sprayed films depends upon the chemical and topographical nature and temperature of the substrate, the chemical nature and concentration of spray solution and its additives. Another factor that affects the growth rate is the spray parameters like scanning speed of the spray head, the distance of the spray head from the substrate, the angle of incidence of the droplet on the substrate etc. The thickness of the film increases almost linearly with spraying time, i.e. with the amount of sprayed solution. In general, the spray pyrolysis process affects the substrate surface. When it is not desirable for the substrate to take part in the pyrolytic reactions, neutral substrates such as glass/quartz, ceramics are employed. The chemical composition of the film is found to depend on the kinetics of the pyrolytic process. Under appropriate conditions, stoichiometric supplied and selenide films and nearly stoichiometric oxide films can be obtained. The stoichiometry of the supplied films does not vary appreciably with the metal-to Sulphur ion ratio in the spray solution for ratios ranging from 1: 1 to 1: 1.5, but the microstructure of the film is strongly influenced by this ratio [29]. But on the other hand, stoichiometry of oxide films is dependent on relatively more complex reactions. In the case of Sn02, the deviation from stoichiometry (i.e., the number of oxygen vacancies) is equal to the number of Sn4+ species reduced to Sn2+ ions, and this is controlled by the water and alcohol content in the spray solution. The oxygen content in the film is also influenced by the rate of cooling of the films after the spray is over, owing primarily to the adsorption of oxygen [30]. The spray deposited films are strongly adherent, mechanically hard, free from pin hole and stable with time and temperature. Post deposition annealing of films generally affects the oxygen dominated electrical properties significantly. Islam and Hakim [31] annealed Sn02 films at 250°C, both in air and vacuum. They observed no change in optical properties, whereas there is a significant improvement in electrical properties. This is due to the oxygen chemisorption desorption mechanisms at grain boundaries. In the present work, we made use of this technique for the preparation of tin oxide thin films and cadmium supplied thin films.

Ion plating (IP)

It is a physical vapor deposition (PVD) process that is sometimes called *ion assisted deposition* (IAD) or *ion vapor deposition* (IVD) and is a version of *vacuum deposition*. Ion plating uses concurrent or periodic bombardment of the substrate, and deposits film by atomic-sized energetic particles. Bombardment prior to deposition is used to sputter clean the substrate surface. During deposition the bombardment is used to modify and control the properties of the depositing film. It is important that the bombardment be continuous between the cleaning and the deposition portions of the process to maintain an atomically clean interface.

In ion plating the energy, flux and mass of the bombarding species along with the ratio of bombarding particles to depositing particles are important processing variables. The depositing material may be vaporized either by evaporation, sputtering (bias sputtering), and arc vaporization or by decomposition of a chemical vapor precursor chemical vapor deposition (CVD). The energetic particles used for bombardment are usually ions of an inert or reactive gas, or, in some cases, ions of the condensing film material ("film ions"). Ion plating can be done in a plasma environment where ions for bombardment are extracted from the plasma or it may be done in a vacuum environment where ions for bombardment are formed in a separate *ion gun*. The latter ion plating configuration is often called Ion Beam Assisted Deposition (IBAD). By using a reactive gas or vapor in the plasma, films of compound materials can be deposited.

Ion plating is used to deposit hard coatings of compound materials on tools, adherent metal coatings, optical coatings with high densities, and conformal coatings on complex surfaces.

The ion plating process was first described in the technical literature by Donald M. Mattox of <u>Sandia National Laboratories</u> (SNL) in 1964

Vacuum evaporation:

It is the most widely used method for preparing stoichiometric thin films, as it is very simple and convenient. Here the only requirement is to have a vacuum environment in which sufficient amount of heat is given to the evaporate to attain the vapor pressure necessary for evaporation. Then the evaporated material is allowed to condense on a substrate kept at a suitable temperature. Deposition consists of three distinguishable steps.

- 1) Transition of the condensed phase (solid or liquid) into the gaseous state.
- 2) Traversal of the vapor from the vapor source to the substrate.
- 3) Condensation of the vapor at the substrate.

When evaporation is made in vacuum, the evaporation temperature will be considerably lowered and the donation of the oxides and incorporation of impurities in the growing layer will be reduced. Evaporation is nominally done at a pressure of 10-5 tort. At this pressure, a straight line path for most of the emitted vapor atoms is also ensured, for a substrate-to-source distance of nearly 10-50 cm. The details of this technique is also available in the standard books mentioned earlier [2-5]. Depending upon the nature of heating there are several types of vacuum evaporation techniques. The most popular types are briefly described in the following section.

Evaporation theory:

For <u>molecules</u> of a liquid to evaporate, they must be located near the surface, they have to be moving in the proper direction, and have sufficient kinetic energy to overcome liquid-phase intermolecular forces. When only a small proportion of the molecules meet these criteria, the rate of evaporation is low. Since the kinetic energy of a molecule is proportional to its temperature, evaporation proceeds more quickly at higher temperatures. As the faster-moving molecules escape, the remaining molecules have lower average kinetic energy, and the temperature of the liquid decreases. This phenomenon is also called evaporative cooling. This is why evaporating sweat cools the human body. Evaporation also tends to proceed more quickly with higher flow rates between the gaseous and liquid phase and in liquids with higher vapor pressure. For example, laundry on a clothes line will dry (by evaporation) more rapidly on a windy day than on a still day. Three key parts to evaporation are heat, atmospheric pressure (determines the percent humidity), and air movement.

On a molecular level, there is no strict boundary between the liquid state and the vapor state. Instead, there is a Knudsen layer, where the phase is undetermined. Because this layer is only a few molecules thick, at a macroscopic scale a clear phase transition interface cannot be seen.

Liquids that do not evaporate visibly at a given temperature in a given gas (e.g., cooking oil at room temperature) have molecules that do not tend to transfer energy to each other in a pattern sufficient to frequently give a molecule the heat energy necessary to turn into vapor. However, these liquids *are* evaporating. It is just that the process is much slower and thus significantly less visible.

Methods of Sputtering:

Sputtering sources often employ magnetrons that utilize strong electric and magnetic fields to confine charged plasma particles close to the surface of the sputter target. In a magnetic field, electrons follow helical paths around magnetic field lines, undergoing more ionizing collisions with gaseous neutrals near the target surface than would otherwise occur. (As the target material is depleted, a "racetrack" erosion profile may appear on the surface of the target.) The sputter gas is typically an inert gas such as argon. The extra argon ions created as a result of

these collisions lead to a higher deposition rate. The plasma can also be sustained at a lower pressure this way. The sputtered atoms are neutrally charged and so are unaffected by the magnetic trap. Charge build-up on insulating targets can be avoided with the use of **RF sputtering** where the sign of the anode-cathode bias is varied at a high rate (commonly 13.56 MHz).^[4] RF sputtering works well to produce highly insulating oxide films but with the added expense of RF power supplies and impedance matching networks. Stray magnetic fields leaking from ferromagnetic targets also disturb the sputtering process. Specially designed sputter guns with unusually strong permanent magnets must often be used in compensation.

1. A) Ion-beam sputtering:-

Ion-beam sputtering (IBS) is a method in which the target is external to the <u>ion source</u>. A source can work without any magnetic field like in a <u>hot filament ionization gauge</u>. In a <u>Kaufman</u> source ions are generated by collisions with electrons that are confined by a magnetic field as in a magnetron. They are then accelerated by the electric field emanating from a grid toward a target. As the ions leave the source they are neutralized by electrons from a second external filament. IBS has an advantage in that the energy and flux of ions can be controlled independently. Since the flux that strikes the target is composed of neutral atoms, either insulating or conducting targets can be sputtered. IBS has found application in the manufacture of thin-film heads for <u>disk drives</u>. A pressure gradient between the ion source and the sample chamber is generated by placing the gas inlet at the source and shooting through a tube into the sample chamber. This saves gas and reduces contamination in <u>UHV</u> applications. The principal drawback of IBS is the large amount of maintenance required to keep the ion source operating.^[5]

2. b) Reactive sputtering:-

In reactive sputtering, the sputtered particles undergo a chemical reaction before coating the substrate. The deposited film is therefore different from the target material. The chemical reaction that the particles undergo is with a reactive gas introduced into the sputtering chamber such as oxygen or nitrogen; oxide and nitride films are often fabricated using reactive sputtering. The composition of the film can be controlled by varying the relative pressures of the inert and reactive gases. Film stoichiometry is an important parameter for optimizing functional properties like the stress in Six and the index of refraction of six.

3. c) Ion-assisted deposition:-

In ion-assisted deposition (IAD), the substrate is exposed to a secondary ion beam operating at a lower power than the sputter gun. Usually a Kaufman source, like that used in IBS, supplies the secondary beam. IAD can be used to deposit <u>carbon</u> in <u>diamond-like</u> form on a substrate. Any carbon atoms landing on the substrate which fail to bond properly in the diamond crystal lattice will be knocked off by the secondary beam. <u>NASA</u> used this technique to experiment with depositing diamond films on <u>turbine</u> blades in the 1980s. IAD is used in other important industrial applications such as creating carbon surface coatings on <u>hard disk</u> platters and hard transition metal nitride coatings on medical implants.

4. d) <u>High-target-utilization sputtering (Hiatus):-</u>

Sputtering may also be performed by remote generation of a high density plasma. The <u>plasma</u> is generated in a side chamber opening into the main process chamber, containing

the target and the <u>substrate</u> to be coated. As the plasma is generated remotely, and not from the target itself (as in conventional <u>magnetron</u> sputtering), the <u>ion</u> current to the target is independent of the voltage applied to the target.

5. e) <u>High-power impulse magnetron sputtering (Hippies):-</u>

Hippies is a method for physical vapor deposition of thin films which is based on magnetron sputter deposition. Hippies utilizes extremely high power densities of the order of kW/cm^2 in short pulses (impulses) of tens of microseconds at low duty cycle of < 10%.

6. f) Gas flow sputtering:-

Gas flow sputtering makes use of the <u>hollow cathode effect</u>, the same effect by which <u>hollow cathode lamps</u> operate. In gas flow sputtering a working gas like <u>argon</u> is led through an opening in a metal subjected to a negative electrical potential.[6] [7] Enhanced <u>plasma densities</u> occur in the hollow cathode, if the pressure in the chamber *p* and a characteristic dimension *L* of the hollow cathode obey the <u>Panchen's law</u> 0.5 Palm < poll < 5 Palm. This causes a high flux of ions on the surrounding surfaces and a large sputter effect. The hollow-cathode based gas flow sputtering may thus be associated with large deposition rates up to values of a few µm/min.

Reactive sputtering:-

In reactive sputtering, the sputtered particles undergo a chemical reaction before coating the substrate. The deposited film is therefore different from the target material. The chemical reaction that the particles undergo is with a reactive gas introduced into the sputtering chamber such as oxygen or nitrogen; oxide and nitride films are often fabricated using reactive sputtering. The composition of the film can be controlled by varying the relative pressures of the inert and reactive gases. Film stoichiometry is an important parameter for optimizing functional properties like the stress in Six and the index of refraction of six.

Radio frequency or (RF) sputtering

It is a technique that is used to create thin films, such as those found in the computer and <u>semiconductor</u> industry. Like direct current (DC) sputtering, this technique involves running an energetic wave through an inert gas to create positive ions. The target material, which will ultimately become the thin film coating, is struck by these ions and broken up into a fine spray that covers the <u>substrate</u>, the inner base of the thin film. RF sputtering differs from <u>DC</u> <u>sputtering</u> in the voltage, system pressure, sputter <u>deposition</u> pattern, and ideal type of target material.

During the sputtering process, the target material, substrate, and RF electrodes begin in a vacuum chamber. Next, the inert gas, which is usually <u>argon</u>, neon, or krypton, depending on the size of the target material's molecules, is directed into the chamber. The RF power source is then turned on, sending <u>radio waves</u> through the <u>plasma</u> to ionize the gas atoms. Once the ions begin to

contact the target material, it is broken into small pieces that travel to the substrate and begin to form a coating.

Since RF sputtering uses radio waves instead of a direct <u>electron</u> current, it has different requirements and effects on the <u>sputtering system</u>. For instance, DC systems require between 2,000 and 5,000 volts, while RF systems require upwards of 10^{12} volts to achieve the same rate of sputter deposition. This is largely because DC systems involve the direct bombardment of the gas plasma atoms by electrons, while RF systems use energy to remove the electrons from the gas atoms' outer electron shells. The creation of the radio waves requires more power input to achieve the same effect as an electron current. While a common side effect of DC sputtering involves a charge build-up on the target material from the large number of ions in the chamber, overheating is the most common issue with RF systems.

As a result of the different powering method, the inert gas plasma in an RF system can be maintained at a much lower pressure of less than 15 moor, compared to the 100 moor necessary for optimizing DC sputtering. This allows for fewer collisions between the target material particles and the gas ions, creating a more direct pathway for the particles to travel to the substrate material. The combination of this decreased pressure, along with the method of using radio waves instead of a direct current for the power source, makes RF sputtering ideal for target materials that have insulating qualities.

DC sputtering

• In DC sputtering, source of power is DC (Direct Current) type.

• DC power is usually preferred for electrically conductive target materials as it is easy to control DC power.

• Chamber pressure is usually 1 to 100 moor

• It is cheaper technique when large quantities of large substrates are dealt with.

• In this technique, positively charged sputtering gas is accelerated towards the target. This results in ejection of atoms which gets deposited on substrate.



UNIT – II

Thickness measurement and Nucleation and Growth in Thin Film:

Thickness measurement: electrical methods – optical interference methods – multiple beam interferometry – Fizeau – FECO methods – Quartz crystal thickness monitor. Theories of thin film nucleation – Four stages of film growth incorporation of defects during growth.

S.No	Lecture Duration	Topics to be Covered	Support Material/Page
	Penou		NOS
		UNIT-II	
1	1	Thickness measurement and	T1:11-28
		Nucleation and Growth in Thin	
2	1	Thickness measurement: electrical methods	T1:11-28
3	1	optical interference methods	T1:11-43
4	1	Continuation	T1:11-43
5	1	multiple beam interferometry	T1:11-6
6	1	Fizeau	T1:11-7
7	1	FECO methods	T1:11-7
8	1	Continuation	T1:11-7
9	1	Quartz crystal thickness monitor	T1:1-107
10	1	Theories of thin film nucleation	T1:8-6
11	1	Continuation	T1:8-6
12	1	Four stages of film growth	R1:5
		growth.	
13	1	Continuation	R1:5
14	1	Revision	
15	1	Recapitulation and Discussion of Important Questions	
	Total No of Hours	Planned For Unit II=15	

Unit 2

Thickness Measurements

The film thickness being one of the important parameter, which affects the properties of the thin film, is measured by various methods viz., weight difference, interference fringes and ellipsometry method.

Weight difference method

Name of the measurement system itself defines its aspect of calculation of thickness where the weight of the substrate is measured before and after deposition of material hence the weightofmaterialis calculated. But only the weight of material is not significant to be calculated hence it requires knowing the dimensions of deposition also, i.e., area of the substrate. Suppose that 'm' Isa mass of the film deposited onthesubstrate which covers area 'A' cm2, the thickness 't' is calculated by using mass of deposit 'm' and density ' ρ ' of the material. The value pertaining to the bulk material is usually taken for ' ρ ' even though the actual density of thin film is low. The thickness is calculated using the equation [1]

$$t = \left[\frac{m}{A \rho}\right]$$

The mass 'm' of the film deposited was measured by using a single pan sensitive electronic microbalance.

Interference fringes method

When two reflecting surfaces are brought into close proximity, interference fringes are produced, the measurement of which makes possible a direct determination of the film thickness and surface topography with high accuracy [1]. Two types of fringes are utilized for thickness measurements, (a) Fazio methodoffringes of constant thickness using multiple beam and (b) Fringes of equal chromatic order method (FECO). The Fazio fringes of equal thickness are obtained in an optical apparatus of the type shown in Fig. 3.1. The interferometer consists of two slightly inclined optical flats, one of them supporting the film, which forms a step on the substrate. When the second optical flat is brought in contact with the film surface, and the interferometer is illuminated with a parallel monochromatic beam at a normal incidence and viewed with a low-power microscope, dark fringes can be observed which trace out the points of equal air-gap thickness. The two adjacent fringes are separated by/2 (where is the wavelength of light used). If the surfaces of the optical flats are highly reflecting and very close to each other, the reflected fringe system consists of very fine dark lines against a white background with a fringe width which can be made as small as/100. By adjusting the relative positions of the flats to forma wedge-shaped air gap, the fringes can be made to run in straight lines perpendicular to the steps on the opaque film. The fringes show a displacement expressed as a fraction of the $\lambda/2$ fringe spacing gives the film thickness and it can be measured to about tenth of a fringe.

In second method, instead of the air wedge, two parallel plates illuminated with white light are used. Fringes occur at wavelength for which t/is constantsothatresultant spectrumis banded. This method is called as "Fringes of Equal Chromatic Order (FECO)". In reflection,

fringes appear dark on bright background. If one of the plates is covered by a film, a displacement Δ is seen in the nthorder fringe, from which film thickness can be calculated as,

0

$$t = \frac{m}{2 \Delta \lambda} \overset{O}{A}$$

$$\underbrace{Interference Plates}_{Silvered Surfaces together}_{Projector}_{Order m m+1 m+2} \overset{O}{Hite Light Source}$$

(b) FECO

Nucleation theory

In fact, the classicalnucleation theory says nothing about such processes, other than that they are possible. In any case, for a $\$ lm to form on the substrate surface, it is necessary that either nuclei formed by such homogeneous processes are able to grow or that a su±cient number of surface defects are available to serve as sites of heterogeneous nucleation. The mode of $\$ lm formation is determined by the relative values of the various energies involved in the process, and this mode largely determines the eventual structure of the $\$ lm. There are two main comparisons to be considered. One of these contrasts the height of the delusion barrierEdtothe background thermal energy. Fideism large compared to the background thermal energy then surface mobility of ad atoms is very low. Under such conditions, ad atoms more or less stick where they arrive on the substrate surface.

For growth of crystalline ⁻ alms, it is important that'd be less than the background thermal energy so that ad atoms are able to seek out and occupy virtually all available equilibrium sites in the ⁻ Im crystal lattices it grows. This requires the substrate temperature and/or the degree of supersaturation of the vapor to be high enough to insure such mobility.Suppose that this is indeed so and that the adatoms are able to make the sufface.

The other important energy comparison concerns the propensity for atoms of $\[$ Im material to bond to the substrate. This is represented by the magnitude offs, relative to their tendency to bond to other, less well-bound, atomsof Immaterial, asrepresentedbyEf. Two kinds of growth processes can be distinguished, one withers larger in magnitude than Ef,andasecondwiththerelativemagnitudesreversed.IfEfs is the larger of the two energy changes in magnitude, then $\[$ Im growth tends to proceed in a layer by layer mode, as indicated in the schematic diagram in Figure 1.8. Ad atoms are more likely to attach to the substrate surface than to other $\[$ Im material surfaces. Once small stable clusters of ad atoms form on the surface, otheradatoms tend to attach to the cluster at its periphery where they can bond with both substrate and $\[$ Im atoms, thereby continuing the planar growth,. This layer-by-layer $\[$ Im growth mode is often called the Frank—van der Merwe growth mode or FM mode, according to categorization of growth modes proposed by Bauer (1958) on the basis of more macroscopic considerations of surface energy. This alternate point of view will be considered

On the other hand, fief is larger in magnitude than Efs, thenitisenergetically favorable for ad atoms to form three-dimensional clusters or islands on the surface of the substrate. Film growth proceeds by the growth of islands until they coalescence; this type of growth is commonly called theVolmer—Weber growth modeortheVWmodeA third type of growth, which combines features of both the Frank {Vander Merwe and the Volker {Weber modes, is called theStranski—Krastanovgrowth mode or SK mode. In this mode, the ⁻Im material tends to prefer attachment to the growth surface rather than the formation of clusters on the growth surface; that is, Eves is greater in magnitude than Ef.However, after a few monolayers of ⁻Im material are formed and after the structure of the ⁻Im becomes better denned as a crystal in conformity with the substrate, the tendency is reversed. In other words, once the planar growth surface becomes established as ⁻Im material, subsequent ad atoms tend more together into clusters than to continue planar growth. The magnitude ofEfsappears to depend on the thickness of the ⁻Im in the early stages of growth, decreasing from values larger than the magnitude off to values that are smaller. The occurrence of this mode is most likely when the ⁻rest few layers of ⁻Im material are heavily strained due to the constraint of the substrate.

Consequences of Nucleation & Growth of Films

• Grain Structure: Nano to Micro Size; Dense; Porous; Columnar; Granular

• Morphology: Particles; Quantum Dots; Nano-wires, - rods,-tubes,-sponges; Films; Multilayers (Super lattices, Wells...)

• Microstructure: Amorphous; Nano to Micro-Crystalline; Oriented; Epitaxial

- Topography: Atomically smooth to micron scale rough
- Crystal Structure: Normal; Polymorphic; Metastable

• Chemical Structure: Normal; Variable and Extended Solubility; Non-equilibrium structuresOpto-electronic Properties of Micro & Nano-structured Films depend very strongly on nucleation and growth processes and hence on numerous deposition parameters





TEXT BOOK:

1. Meissel. L.T and R. Glang., 2000, Hand book of thin film technology, Tata McGraw Hill, New Delhi.

REFERENCE:

1. Anderson, J.C.2011 Ist edition The use of thin films in physical investigation, Academic press 2. Berry, Hall and Harris.2003, illustrated edition Thin films technology, Van Nostrand Reinhold publishing

3. Chopra, K.L. Ist edition 2004, Thin film Phenomena, Mc Graw hill

4. Chopra, K.L. and Das, S.R Ist edition2013 Thin films solar cells.springer

5. George Hass and others (Ed). Physics of thin films, vol. 12. Academic press 2001

6. Holland, L Ist edition 2004, Vacuum deposition of thin films. Weily Publication

UNIT – III

Electrical properties of metallic thin films:

Sources of resistivity in metallic conductors – sheet resistance - Temperature coefficient of resistance (TCR) – influence of thickness on resistivity – Hall effect and magneto resistance – Annealing – Agglomeration and oxidation.

S.No	Lecture	Topics to be Covered	Support Material/Page Nos
	Period		Material/Page Nos
		UNIT-III	
1	1	Electrical properties of metallic thin films	T1:13-2
2	1	Sources of resistivity in metallic conductors, sheet resistance	T1:13-2 T1:13-5
3	1	Temperature coefficient of resistance (TCR)	T1:13-7
4	1	influence of thickness on resistivity	T1:11-4
5	1	Hall effect and magneto resistance	T1:21-29
6	1	Annealing	T1:13-26
7	1	Agglomeration and oxidation. Transformation	T1:13-30
8	1	Revision	
	Total No of Hours Planned For Unit III=8		

Unit III

Electrical Properties

Knowledge of the electrical properties of semiconductor materials necessary for understanding the factors limiting the performance of solar cells. The electrical properties of interest are the type of carriers, resistivity, and mobility and carrier concentration. Here we describe the commonly used parameters.

Resistivity.

The most commonly used technique for measurement of resistivity of semicondctors is the "four probe method". Four collinear metal probes are placed on the semiconductor. A constant current (I) is passed between the two outer probes and the voltage (V) between the inner two probes is measured. Resistivity is then calculated from the relation

$$\rho = \frac{2\pi S_0 V}{I}$$

Where so is the distance between the probes. Another parameter usually measured in thin film samples is the sheet resistance, which is expressed in Q / D. This is measured using a simple two probe method, selecting a square geometry for the specimen. The sheet resistivity is then calculated by multiplying the sheet resistance with the thickness of the film. The sheet resistance is independent of the size of the square we select.

Electrical Characterization and Four point probe method and resistivity of thin films

The use of thin films as resistors, contacts and interconnections has lead to extensive study of conductivity, temperature dependence, the effect of thermal processing stability and so on. Investigationofthe critical resistivity as a highly structure sensitive properties make it possible to gain insight into the structuralandelectrical properties of the metal films which is important from both the theoretical and practical point of view. The contact methods are most widely used for the measurement of resistivity. These methods include two-point probe, four-point probe and the spreading resistance. The two-point probe method is simple, easy to use and useful for high resistive thinfilms. In this method constant voltage 'V' is applied between two fixed position probesseparation 'd' in cm and current passing through a sample of known dimension (crosssectional area 'A' inis measured with anappropriate currentmeter. For uniformsample, resistivity is given by,

$$\rho = \left(\frac{AV}{Id}\right) \quad \Omega\text{-cm}$$

In case of semiconducting thin films, the resistivity decreases with increase intemperature. The thermal activation energies 'Ea' are calculated by using equation

$$\rho = \rho_0 \exp\left(\frac{-E_a}{KT}\right)$$

where symbols have their usual meanings. Hence we plot Log (ρ) versus 1/T and itsslope leads to the estimation of activation energy. The experimental setup used to study the variation of resistivity with temperature schematically shown in Fig. 3.6. The brass plate of size 10 cm ×0.5 cm is grooved atthe bottomside soas to fit theheating element (Toni, 60 watt) parallel to the length of the plate, in order to achieve the uniform temperature. The sample is mounted on the topof the plate. The thin film of size 1 ×1 cm2on the glass substrate is used for theresistivity measurement. Silver paste was applied for making the good ohmic contacts to the film. A mica sheet was used between the filmand thebrass plate to provide the insulation. The temperature is measured with chromel-alumel thermocouple, which is fixed at the center of the sample. The temperature was recorded on digital panel meter (0to 199.9 mV range) (DPM) supplied by Omega Electronics, Jaipur. Aplab power supplyis used for passing current through the film and the current was measured with MECOmade (MIC-60E) digital currentmeter.



Fig. 3.6 Schematic circuit diagram for the measurement of electrical resistivity of thin film [Lab. setup]

Annealing Process

In the present work of junction fabrication, we prepared p-CdS samplesby the thermal annealing of copper deposited over n-CdS under high vacuum. Since this process forms the major part of our work, it needs an elaboration. The annealing chamber was made of a glass tube over which nichromewire was wound uniformly over the entire length of the tube. Length of the glasstube is such that three samples (5 x 1.2 cm2) can be placed well inside the tube, so that a uniform heating was ensured for the samples. The tube was placed in the vacuum coating chamber and the pressure was measured using a penninggauge (Hindhivac, model STA 6P4M). Temperature was controlled by controlling the current through the nichrome wire connected to a variac and was measured using a Chromel-alumel thermocouple. The heating and cooling ratefor all the annealing was kept at the rate of 2° C/minute.

TEXT BOOK:

1. Meissel. L.T and R. Glang., 2000, Hand book of thin film technology, Tata McGraw Hill, New Delhi.

REFERENCE:

1. Anderson, J.C.2011 Ist edition The use of thin films in physical investigation, Academic press

2. Berry,Hall and Harris.2003,illustrated edition Thin films technology,Van Nostrand Reinhold publishing

3. Chopra, K.L. Ist edition 2004, Thin film Phenomena, Mc Graw hill

4. Chopra, K.L. and Das, S.R Ist edition2013 Thin films solar cells.springer

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

Transport properties of semiconducting and insulating Films:

Semiconducting films; Theoretical considerations - Experimental results – Photoconduction – Field effect thin films – transistors, Insulation films Dielectric properties – dielectric losses – Ohmic contracts – Metal – Insulator and Metal – metal contacts – DC and AC conduction mechanism .

S.No	Lecture Duration	Topics to be Covered	Support Material/Page Nos
	Period		
		UNIT-IV	
1	1	Transport properties of semiconducting and insulating Films	T1:10-19
2	1	Semiconducting films, Theoretical considerations ,Experimental results	T1:10-19
3	1	Photoconduction ,Field effect thin films	T1:20-8 T1:20-2
4	1	transistors, Insulation films Dielectric properties	T1:16-28
5	1	dielectric losses	T1:16-3
6	1	Ohmic contracts	T1:14-6
7	1	Metal ,Insulator and Metal, metal contacts	T1:14-5
8	1	DC and AC conduction mechanism	T1:16-5 T1:16-11
9	1	Revision	
	Total No of Hou	rs Planned For Unit IV=9	

Unit IV

Transport Properties:

Surface transport phenomena are well known to have a strong influence on the electronic properties of bulk semiconductors. When transport takes place through thin specimens, the carriers are being subjected to considerable scattering by the boundary surface in addition to normal bulk scattering. This additional scattering will reduce the effective carrier mobility below the bulk value and will thus give rise to quantum size effects. A study of these size effects can yield information on the electronic structure of a surface and is therefore of considerable fundamental and practical importance. The sephenomena play an important role in the transport properties of semiconducting film of about $1 \square$ m thickness and having carrier concentration upto 1018 cm-3. Surface transport phenomena in bulk semiconductor have received much attention in recent years. An excellent review of the subject is given by Pulliam et al. [34]. The important transport properties i.e. electrical resistively, thermoelectric power (TEP) are discussed below.

a) <u>Electrical Conductivity:</u>

The use of thin films as resistors, contacts and interconnections has lead temperaturedependence, toextensive study of conductivity, its the effect of thermalprocessing stability and so on. Investigations of the electrical resistivity as a highly structure sensitive properties make it possible to gain insight into the structural and electrical properties of the metal film which is important from both the theoretical and The contact techniques are most widely used for practical point of view. themeasurement of resistivity. These techniques include two-point probe, four point probeand the spreading resistance methods. The two-point method is simple and easy to use. In this technique a constant current I is passed through a sample of known dimensions(crosssectional area 'A'). And the d.c. voltage 'V' between two fixed position probes(separation'd') measured either with impedance voltmeter or potentiometrically. Foruniform sample resistively is given by

$\rho = (A/I) (V/d)$

In case of semiconducting thin films, the resistivity decreases with increase intemperature. The thermal activation energies 'Ea' are calculated by using followingrelation:

$$\sigma = \sigma_o \exp^{(-\Delta E / \kappa T)}$$

Where $\Box E$ is the activation energy for the conductionis Boltzmann constant and is the pre exponential constant depending on the material. The two brass plates of the size 10 x 5 x 0.5cm are grooved at the centre to fix the heating elements. Two strip heaters (65 Watts)were kept parallel in between these two brass plates to achieve uniform temperature. The two brass plates are then screwed to each other. The sample was mounted on the upper brass plate at the centre. To avoid the contact between the film and the brassplate, a mica sheet was placed

between the film and brass plate. The area of the film was defined and silver emulsion (paste) was applied to ensure good electrical contact tothe films. The working temperature was recorded using a Chromel-Alumel thermocouple(24 gauge) fixed at the centre of the brass plates. Testronix model 34 C (power supplyunit) was used to pass the current through the sample. The potential drop across thefilm was measured with the help of Meco 801 digital multimeter and current passedthrough the sample was noted with a sensitive 4 digit picoammeter (Scientificequipment, Roorkee DPM 111). The measurements were carried out by keeping the filmsystem in a light tight box, which was kept at room temperature.



Fig. 2.18 b Cross sectional view of of electrical conductivity measurement unit.

b) Thermoelectric Power (TEP):

If some metal contacts are applied to the two ends of a semiconductor and if onejunction is maintained at higher temperature than the other, a potential difference isdeveloped between the two electrodes. This thermoelectric or Seebeck voltage isproduced party because

- i) The majority carriers in the semiconductor diffuse from hot to cold junction, thus giving potential difference between the ends of the specimen. This voltage builds upto avalue such that the return current just balances the diffusion current when a steadystate is reached.
- ii) Other part which contributes to the thermoelectric voltage is the contact potential difference between metal and emiconductor, which occurs at two junctions.

In the semiconductor, if the charge carriers are predominantly electrons, the coldjunction becomes negatively charged and if the charge carriers are positive holes, the cold junction becomes positively charged. The magnitude of the developed voltage is proportional to the difference in temperature between the hot and cold junction, if the temperature difference is small. From the sign of the thermoelectric voltage it is thuspossible to deduce whether a given specimen exhibits n-or p-type conductivity. The thermoelectric power (TEP), which is defined as the ratio of thermallygenerated voltage to the temperature difference across the piece of semiconductor, gives the information about the type of carriers in the semiconductor.

Thermoelectric power measurement apparatus consist of two brassblocks. One brass block was used as a sample holder-cum-heater. Other brass blockwas kept at room temperature. The hot and cold junction was kept thermally isolated byinserting an insulated barrier between the junctions. The size of the film used in thisstudy was 40 mm x 12.5 mm x 1.35 mm on amorphous glass substrates, were fixed ontwo brass blocks. Chromel – Alumel thermocouples (24 gauze) were used to sense theworking temperature. A 65 watt strip heater was used for heating the sample. Thetemperature of the hot junction was raised slowly from room temperature, with a regularinterval of 10 K. the thermo emf was noted up to the highest temperature of 500 K.Silver paste contacts were made to films with copper wire. A backellite box was used forproper shielding of the TEP unit, which also minimises to some extent, thermal radiationlosses. The mean temperature was measured with a Meco 801 digital multimeter while the differential thermal gradient and thermoelectric voltage were measured with digitalTestronix microvoltmeter.



Fig 2.19 a. Photograph showing the thermoelectric power measurement



Fig. 2.19 b. Cross sectional view of the thermoelectric power measurement unit.

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4. Chopra, K.L. and Das, S.R Ist edition2013 Thin films solar cells.springer

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

Optical properties of thin films and thin films solar cells:

Thin films optics –Theory – Optical constants of thin films – Experimental techniques – Multilayer optical system – interference filers – Antireflection coating, thin films solar cells: Role, Progress, and production of thin solar cells – Photovoltaic parameter, thin film silicon (Poly crystalline) solar cells : current status of bulk silicon solar cells – Fabrication technology – Photo voltaic performance: Emerging solar cells: GaAs and CulnSe2.

S.No	Lecture Duration Period	Topics to be Covered	Support Material/Page Nos
		UNIT-V	
1	1	Thin films optics	R4:10 T1:8-3
2	1	Theory ,Optical constants of thin films	R4:10
3	1	Experimental techniques	R4:13 T1:49-54
4	1	Multilayer optical system	R4:60 T1:1-71
5	1	interference filers	R4:60 T1:15-1
6	1	Antireflection coating, thin films solar cells: Role, Progress, and production of thin solar cells	T1:11-13 T1:11-21
7	1	Photovoltaic parameter, thin film silicon (Poly crystalline) solar cells; current status of bulk silicon solar cells	R4:391 T1:14-1
8	1	Fabrication technology	R4:391
9	1	Photo voltaic performance: Emerging solar cells: GaAs and CulnSe2.	R4:403 T1:20-1
10	1	Continuation	R4:417 T1:18-3
11	1	Revision and Old Question paper Discussion	
12	1	Revision and Old Question paper Discussion	
13	1	Revision and Old Question paper Discussion	
	Total No of	Hours Planned for unit V=13	
Total Planned Hours	60		

Unit V

Optical Properties

Optical properties of solid emanate from the interaction swith electromagnetic waves and are manifested in optical frequencies. The effect of such interaction in optical frequencies results in optical behavior. Optical properties of filmhave been studied extensively primarily because of there application in various optical and optoelectronic devices. It has been found that there is considerable deviation of optical parameters from that of the bulk material. The optical study of a solid, concern not only with physical phenomenon like reflection, refraction, absorption, transmission and interference of lightbut also on interaction of photon energy with matter and consequent change in thereelectronic states. The study of optical properties of solids helps in understanding of electronic and atomic structure of these materials [24]. Absorption studies provide simple means for the evaluation of absorption edge, optical energy band, optical transition that may be direct or indirect, allowed or forbidden and also of the nature of the solid material. Asimple way to determine the optical properties of solid is by illuminating the sample with light and then measure the reflection, transmittance or absorbance as afunction of photon energy. This was experimented by spectroscopic methods.

<u>Thin Film Solar Cells</u>

(A Status Review)

SOLAR Cell:PHOTOVOLTAICS

- Direct Conversion of light into electrical energy is called PHOTOVOLTAICS (PV)
- Photovoltaic devices which convert solar energy into electricity are called SOLAR CELLS
- Two electronically dissimilar materials (with different free electron densities) brought together to form a junction with a barrier form a PV device. Typical examples are :
 - $metal_1$ -oxide-metal_2
 - metal-semiconductor (Schottky)
 - p-type semiconductor-n-type semiconductor (Homojunction)
 - n+-n semiconductor
 - p-type semiconductor⁽¹⁾-n-type semiconductor⁽²⁾ (Heterojunction)
 - p- (Insulator)-n
 - $(p-i-n)_1-(p-i-n)_2-p-i-n)_3$ (Multijunction)



JUNCTION FORMATION ABILITY HIGH QUANTUM EFFICIENCY LONG DIFFUSION LENGTH LOW RECOMBINATION VELOCITY ABUNDANT,CHEAP & ECO-FRIENDLY MATERIAL · CONVENIENCE OF SHAPES AND SIZES · SIMPLE AND INEXPENSIVE <u>INTEGRATED</u> PROCESSING/MANUFACTURABILITY · MINIMUM MATERIAL / WATT · MINIMUM ENERGY INPUT/ WATT · ENERGY PAY BACK PERIOD < 2 YEARS · HIGH STABILTY and LONG

LIFE (> 20 Years) \cdot COST (<

1\$/Watt)

POSSIBLE Solar Cell Materials Single Elements:

Si (epi, mc, nc, mixed) Carbon (nanotubes, DLC)

Binary alloys / Compounds:

Cu₂S, Cu₂O Cu-C, CdTe, CdSe,

GaP, GaAs, InP,ZnP, a-Si : H, Dye coated TiO₂

Ternary (+) Alloys / Compounds:

Cu-In-S, Cu-In-Se, Cu-Zn-S, CdZnSe, CdMnTe, Bi-Sb-S,

Cu-Bi-S, Cu-Al-Te, Cu-Ga-Se, Ag-In-S, Pb-Ca-S,

Ag-Ga-S, Ga-In-P, Ga-In-Sb ,and so on.

Organic Materials:

Semiconducting Organics / Polymers and Dyes

Spectral response of solar cells



Crystalline Silicon : Present Scenario

- Efficiency of single crystal Si cells (Laboratory) has been rising steadily to $\sim 25\%$ as a result of better understanding of the junction properties and innovations in cell design and fabrication technologies.
- Efficiency gap between best laboratory cells, submodules/modules, and mass produced modules varies with the maturity of technology and can be at least 10% lower at every step so that the manufactured cell may be as low as 50% of the efficiency of

the best laboratory cell.

The world PV production of ~ 7900 MW in FY 2009 is primarily (~ 93%) based on crystal and polycrystalline silicon. single,

With increasing production of Si-PV from 200 kW in 1976 to 6900 MW in 2008, the cost of solar cells has decreased from \$100 to about \$3/Wp

- With the existing technology and the material cost, the cost of Si cells can not be decreased significantly unless major innovations in the production of appropriate quality silicon I thin sheets take place.
- Present day technology uses 8" or larger pseudo square of $\sim 200 \mu$ m thickness, with an efficiency of ~ 15-16%. The energy (16-5 kWH/Wp) pay back period of such cells is ~3-
- years. The module life is about 25 years 4
- Specially designed silicon solar cells with efficiency ~ 18-20% are being manufactured on a limited scale for special applications (e.g. for concentration).

- Polycrystalline silicon solar cells with efficiency ~ 12-14% are being produced on large scale.
- Specially designed thin(~ 20 m) films silicon solar cells with

efficiency ~ 12% have been fabricated on a lab scale . Production of hybrid thin film Si cells on MW scale is being pursued

Solar module production for different technologies



WHY THIN FILM SOLAR CELLS ?

- ✓ SMALL THICKNESS REQUIRED DUE TO HIGH ABSORPTION, SMALL DIFFUSION LENGTH & HIGH RECOMBINATION VELOCITY
- ✓ MATERIALS ECONOMY, VERY LOW WEIGHT GHT PER UNIT POWER

□ VARIOUS SIMPLE & SOPHISTICATED DEPOSITION TECHNIQUES

□ A VARIETY OF STRUCTURES AVAILABLE : AMORPHOUS, PLOYCRYSTALLINE, EPITAXIAL

✓ TOPOGRAPHY RANGING FROM VERY ROUGH TO ATOMICALLY SMOOTH □DIFFERENT TYPES OF JUNCTIONS POSSIBLE –HOMO, HETERO, SCHOTTKY, PEC

TANDEM AND MULTI JUNCTION CELLS POSSIBLE

□IN-SITU CELL INTEGRATION TO FORM MODULES

COMPATIBILITY WITH SOLAR THERMAL DEVICES

• TAILORABILITY OF VARIOUS OPTO-ELECTRONIC PROPERTIES (e.g; Energy Gap ,Electron Affinity ,Work function ,Graded Gap ,etc)

Thin Film Cu₂S –CdS Cell

- One of the simplest solar cell to produce with simple chemical conversion technique
- Highest efficiency obtained ~10 %
- Large scale production of modules with ~5% efficiency demonstrated during 70's
- Stability of cells due to cuprous-cupric conversion remained an issue
- Due to the emergence of higher efficiency Si cells, this cell lost the battle of survival
- Revival of this cell with suitable modifications is a possibility

Crystalline states of Si: Long range or short range order of atoms





Uncoordinated atoms and broken

c-Si & Poly-Si bonds (called **dangling bonds** are

characteristics of a-Si

a-Si – amorphous Si

a-Si:H – amorphous hydrogenated Si Hydrogen passivates the uc-Si:H – microcrystalline Si (hydrogenated)dangling bonds in a -Si:H. Almost

any impurity can be added to this open structure to obtain asuitable semiconducting behaviour

Absorption coefficient of Si can change with the crystalline state

Different Eg

Why Amorphous Silicon as a Photovoltaic Material?



UNI-S single/tandem/triple junction solar cells

Triple junction a-Si:H/SiGe:H/nc-Si:H solar cell

Area: 0.25 cm^2





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