

### INTRODUCTION

Solar energy is a very large inexhaustible source of energy. The power from the Sun intercepted by the earth is approximately  $1.8 \times 10^{11}$  MW, which is many thousands of times larger than the present consumption rate of earth from all commercial energy resources. Thus in principle, solar energy could supply all the present and future energy needs of the world on a continuing basis. It is the most promising unconventional energy source and is economical and environmentally clean.

There are mainly two routes of utilization of solar energy; viz., thermal and photovoltaic. The efficiency of solar energy converting devices is very low (1%). Photovoltaic technology which converts sunlight to electricity is a versatile power source which could be used for many applications. The cleanest and most direct efficient way to utilize the solar energy is the direct conversion of light energy to electrical energy through photovoltaic devices called solar cells. This can be achieved at low cost and with high conversion efficiency. Basically, photovoltaic conversion occurs through three separate processes;

1. The absorption of light to create electron-hole pair in the appropriate semiconductor.
2. Collection and separation of these carriers by internal field.
3. Distribution to an external load.

To obtain higher output voltage, individual solar cells are frequently cascaded in series and / or parallel combinations.

## 1.1. ESSENTIALS OF SOLAR CELLS

Essentially a solar cell consists of a p-n junction of the same material (homo-junction) or two different materials (hetero-junction). The p-type material is the absorber of the incident solar radiation and the n-type material serves as a window to provide the junction field. The output voltage of the photovoltaic cell is decided by the band gap of the p -type material.

In recent years, thin film materials and their associated techniques offer an extremely attractive approach towards the production of efficient and cost effective solar cells. However, high conversion efficiency is possible only by employing suitable materials II –VI semi-conducting compounds arouse a lot of practical interests owing to their unique properties which include their photosensitivity to electromagnetic and particulate radiation, almost cent percent quantum yield of radioactive recombination ability. It is also possible to vary widely the band gap energy and hence the spectral range of photosensitivity. Commercial production of devices based on these group compounds, the scientific and technological improvements are so advanced that the thin polycrystalline samples could be prepared with reproducible properties much more accurately than those of single crystals [1].

In general, in the fabrication of solar cells, absorption and occurrence of photons with energy greater than the band gap ( $E_g$ ) of the materials used. Obviously for greater carrier generation and higher photocurrent, the band gap of the material ( $E_g$ ) should be small accompanied with high absorption coefficient in the visible portion of the solar spectrum. However, to deliver higher  $E_g$  more will be the open circuit voltage ( $V_{oc}$ ) available from the cell. Hence, to develop an efficient solar cell with high photocurrent ( $I_{sc}$ ) and high open circuit voltage  $V_{oc}$ , a combination of

low band gap absorber, 'p' type and high band gap window, 'n' type semiconductor should be used as hetero junctions. Thin films of group II-VI compound semiconductors have prominent place in the commercial solar systems employing photovoltaic and photo electrochemical conversions.

## 1.2. ROLE OF THIN FILMS IN SOLAR CELLS

Some important features of thin films in relation to technology are: The band gap of the base material is one of the principal parameters that determine the performance of a solar cell. Photons with energies less than the band gap ' $E_g$ ' does not get absorbed in the material and hence cannot contribute to the short circuit current. Thus, a very large band gap leads to less conversion of incident light into electricity. On the other hand, a very small band gap will lead a reduced open circuit voltage, 'Voc' developed across the device. Hence, an optimum range of band gap is desirable. The solar spectrum, shown in Fig.1.1 which has some maximum region and a great deal of structure due to various atmospheric absorption bands and also to be taken into consideration while calculating the optimum band gap.

Fig.1.2 shows a typical set of homo-junction device under AMO conditions [2]. The curve (a) represents the solar cell with ideal behaviour ( $n=1$ ) and curve (b) for  $n=2$ , generation recombination - mechanisms dominate.

Fig.1.3 shows the maximum efficiency as a function of absorber energy gap for various window layers. The window is a larger band gap semiconductor that provides the junction with the active absorber but does not itself absorb any significant quantity of photons. Calculations based on the data in the above figure should be taken as guidance for selecting ranges of optimum band gaps in solar cell materials [3].

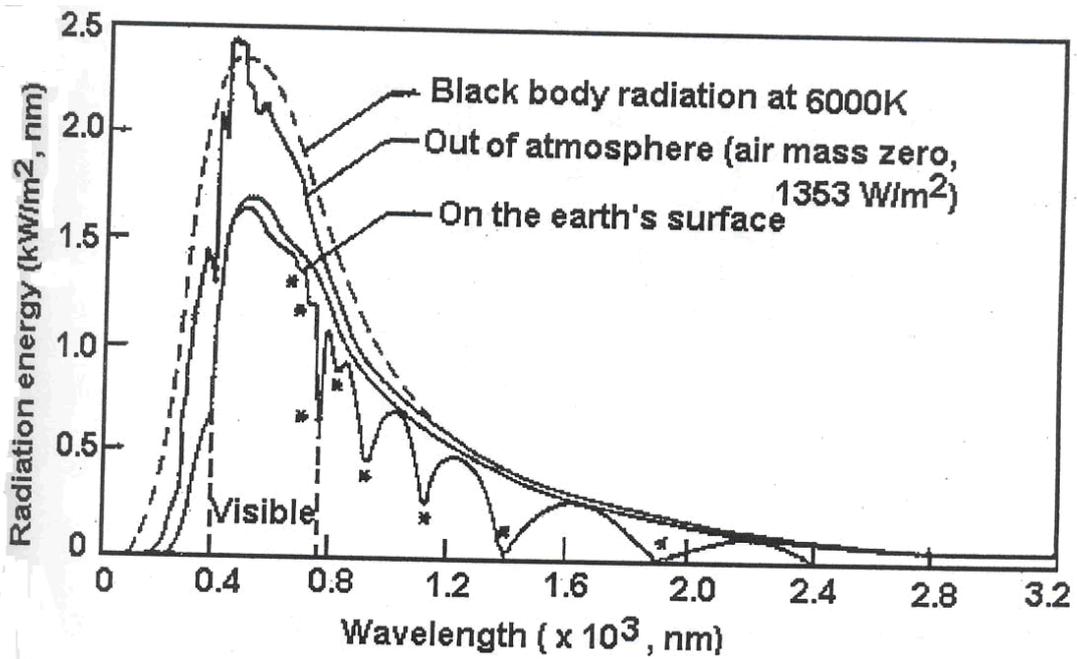


Fig.1.1 Solar energy density at various wavelengths

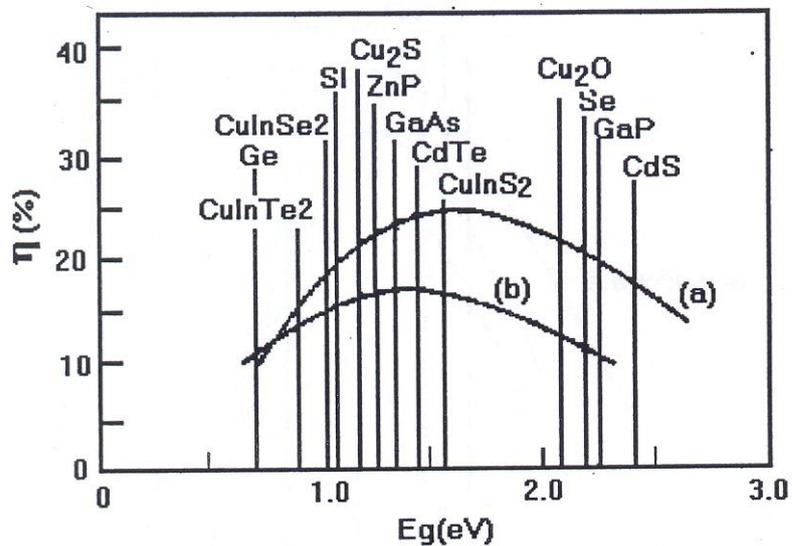


Fig.1.2 Theoretical efficiencies of homo-junction solar cells as a function of energy gap for (a) ideal diode when  $n=1$  and (b) non-ideal diode with  $n=2$  under AMO conditions.

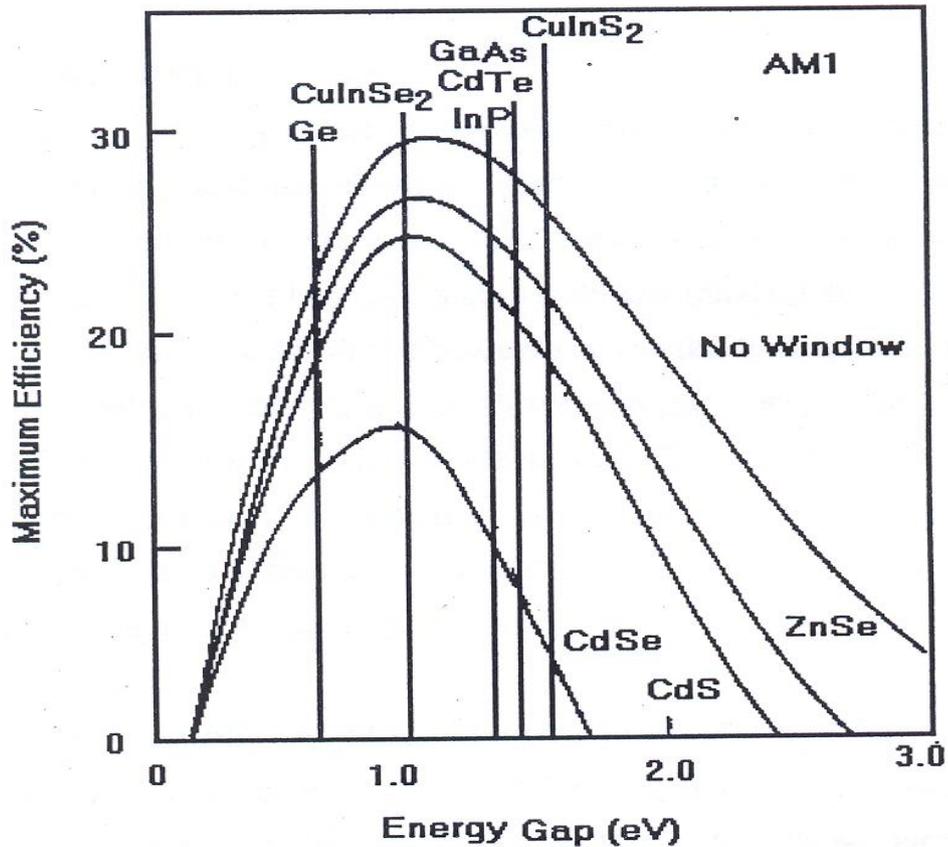


Fig.1.3 Theoretical efficiencies of hetero-junction cells as a function of energy gap

### 1.3. APPLICATIONS OF METAL OXIDE THIN FILMS

#### 1.3.1. Solar cells

The direct conversions of light energy into electrical energy through photovoltaic devices are called solar cells. This conversion can be achieved at low cost with desirable conversion efficiencies.

#### 1.3.2. Electrical conductors

Metal films are the most common electrical conductors. They may be used as “blanket” metallization. Conductor lines are not only used in hybrid microcircuit technology but also in the manufacture of semiconductor devices. The electrical

conductors are often multilayer films (stacks) with each distinct functional layer. For example, the conductor films stack might have the composition; glass – Ti-Pd-Cu-Au. In this, titanium forms “glue” layer, the palladium to provide corrosion resistance, whereas the copper facilitates electrical conductivity and the gold provides corrosion protection. In the manufacturing of semiconductor devices, metals are used as “vias” for establishing electrical contact between different layers. Blanket metallization is used to provide electromagnetic interference (EMI) and radio frequency interference (RFI). In order which is also used as Shielding on structures such as the plastic cases for cellular phones, electrodes for rigid and flexible capacitor electrodes, and surfaces for radar “chaff”.

In general, metal nitride, carbide and silicide films are electrically conductive ( $\text{Si}_3\text{N}_4$  and  $\text{AlN}$  are important exceptions). In some applications, films of these refractory materials are used to provide diffusion barriers between materials. For example, in semiconductor metallization, aluminium or gold electrode materials will diffuse into silicon during high-temperature processing. An electrically conductive titanium nitride film reinforced on the silicon surface before the deposition of the metal electrode will prevent the diffusion. Generating stable, electrically conductive, non-rectifying and metal semiconductor contacts of metals or metal-silicide compounds are important aspects of thin film resistor technology. Non transparent, electrically conductive oxides such as chromium trioxide ( $\text{Cr}_2\text{O}_3$ ), lead oxide ( $\text{PbO}$ ), and ruthenium oxide are used as electrodes in high-temperature oxidizing atmospheres.

Superconductors are materials that have close to zero electrical resistivity below some critical temperature ( $T_c$ ). Low-  $T_c$  (less than 10 K) superconductors are often metals. A typical high-  $T_c$  (greater than 50 K) superconductor’s material is a

mixture of oxides ( $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  oxides). High-  $T_c$  superconductor thin films often deposited by laser ablation in vacuum.

### **1.3.3. Transparent electrical conductors**

Transparent conductive oxide (TCO) films, such as oxides of indium, tin, zinc and an alloy of indium and tin (ITO), have numerous applications such as heaters on windows for defrosting, antistatic coatings on display screens, electrodes on flat panel displays and electro-chromic devices, and electrodes on both flexible (resistive screen) and rigid (capacitive screen) touch screen. Electrical resistivity of the TCO films can vary from greater than 1000 ohms per sq. cm to less than 10 ohms per sq. cm with good optical transmission on glass substrate.

### **1.3.4. Electrical insulators**

Electrically insulating films are used to isolate electrically conducting components in semiconductor devices and as a dielectric within capacitors. Common insulator film materials are silicon dioxide ( $\text{SiO}_2$ ), aluminium trioxide ( $\text{Al}_2\text{O}_3$ ), tantalum pentoxide ( $\text{Ta}_2\text{O}_5$ ), silicon nitride ( $\text{Si}_3\text{N}_4$ ) and aluminium nitride (AlN). Interposing a thin oxide film between a metal film and a semiconductor allows the formation of technologically important metal-oxide-semiconductor (MOS) devices. Thick coatings of  $\text{SiO}_2$ , with its low coefficient of thermal expansion can be RF-sputter deposited. Insulating layers of silicon  $\text{SiO}_2$ , silicon nitride ( $\text{Si}_2\text{N}_3$ ), and glass are deposited by PECVD for the encapsulation and insulation layers in semiconductor processing.

### **1.3.5. Optical films**

Optical films are films that affect the optical transmission or reflection of a surface. They are generally alternating layers of materials like Ge, Si,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{SiO}$ ,  $\text{CeO}_2$  and  $\text{MgF}_2$ , having higher indices of refraction. A major application is the anti-reflection (AR) coatings on lenses. Optical film stacks can be used as optical

filters. Neutral density or gray filters reduce the light intensity equally for all wavelengths; broadband filters affect the transmission of radiation over a wide wavelength range, while narrow or monochromatic filters affect transmission over a narrow wavelength region. An example of a broadband filter is an “edge filter” that “cuts off” the ultraviolet (UV) emitted by a mercury vapour lamp. Examples of narrow-band filters are the color filters used in photography and in projectors.

Some film stacks are special type of optical film that has a colour that is related to the angle-of-observation. These films allow holographic-like imaging. These OVID films are used as security devices to prevent counterfeiting. These films are also, used as decorative films when an outgrowth of the interference-coloured films pulverized as pigments.

### **1.3.6. Reflector coatings**

Metal films are widely used for reflector surfaces. Silver is often used when corrosion is not a problem, such as for back-surface mirrors. Aluminum can be used either as a front-surface or back-surface reflector. Often, aluminized front-surface reflectors, such as headlight reflectors, are over coated with a protective polymer film (top coat). Chromium is used on front-surface reflectors when corrosion is a problem even though its reflectivity in the visible (60%) is less than that of aluminum (>90%). Reflector films are also used in numerous commonly encountered applications, such as on compact discs for video and music storage, lamp reflectors, and visual mirrors such as rearview mirrors for cars. In some cases, multilayer films, similar to multilayer optical films, are used selectively to reflect certain wavelengths and not others. Examples are “cold mirrors” that reflect the visible radiation but not the infrared wavelength and “heat mirrors” that reflect the infrared but not the visible.

Heat mirrors are used to raise the internal temperature of halogen lamps. Whereas cold mirrors are used to reduce the heat of stage lighting on actors.

### **1.3.7. Hard and wear-resistant coatings**

Hard coatings are often called as metallurgical coatings and also as topological coating. The hard coatings are used to increase the cutting efficiency and operational life of cutting tools and to maintain the dimensional tolerance of components used in applications where wear can occur such as injection moulds. In addition, the coatings can act as a diffusion barrier where high temperatures are generated by motion between surfaces or corrosion protection in aggressive environments. There are various classes of hard coating materials. They include ionically bonded metal oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  and  $\text{TiO}_2$ ), covalently bonded materials (SiC, boron carbide diamond-like-carbon, TiC, CrC, mixed carbide, nitride and carbonitride compounds and cubic boron nitride), and also some metal alloys of the type CoCrAlY, NiAl, NiCrBSi . In some cases, the coatings may be layered to combine properties.

Hard coatings are also used to minimize fatigue-wear, such as found in ball bearing. Wear-resistant coatings may be applied to surfaces where there is a light or periodic load. For example, hard coatings are deposited on plastics to improve scratch resistance. In some cases, wear coatings, such as  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$  may be applied to already hard surfaces such as glass to increase the scratch resistance.

### **1.3.8. Electrically active films**

Doped silicon films are used in semiconductor devices and these films are often deposited by a very sophisticated PVD evaporation technique. Amorphous silicon for solar cells is deposited by PECVD on webs and rigid substrates. Electrochromic films, which change optical transmission on the application of a voltage,

depend on the diffusion of a mobile species in the film under an electrical field. Films of a material such as selenium can become electrically charged when exposed to light. Such films are used to hold the toner in photocopying machines.

### **1.3.9. Magnetic storage media**

Magnetic materials are classified as “hard” or “soft” depending on how hard it is to magnetize, demagnetize, or “switch” the magnetic field. Soft magnetic materials, such as the perm alloys (Fe : 40 to 80% Ni) and  $Y_2Fe_5O_{12}$  (garnet) are used in memory storage devices where data are changed often. Hard magnetic materials such as  $Fe_3O_4$ , Co-Ni-W, Co-Re and Gd-Tb-Fe are used in more permanent recording media such as audio tapes. Various techniques used to define the magnetic domains that act as storage sites.

### **1.3.10. Corrosion protective coatings**

Protection from an aggressive chemical environment can be accomplished in several ways. The surface can be coated with an inert material or with a material that forms a protective surface after reacting with the environment or with a material that will be sacrificially removed to protect the underlying material. Tantalum, Platinum and carbon are inert in many chemical environments. For example, carbon coatings are used on metals that are implanted in the human body to provide compatibility. In the aerospace industry, parts are coated with aluminum by PVD process to prevent galvanic corrosion of dissimilar materials in contact.

Chromium, Aluminum, Silicon and the MCrAlY (where M is Ni, Co, Fe) alloys will react with oxygen to form a coherent protective oxide layer on the surface. If the metal ions (Fe, Cu) diffuse more rapidly than the oxygen through the oxide, a thick oxide will be formed on the surface. If the oxygen diffuses more rapidly through the oxide than the metal ions (Al, Si, Ti, Zr metals), oxidation will occur at the interface

and thin oxide film will be formed. The MCrAlY alloy coatings are used as protective coatings on aircraft engine turbine blades. Vacuum cadmium plating has the advantage over electroplated cadmium in that there is no possibility of hydrogen embrittlement of high-strength steel.

### **1.3.11. Solid film lubricants /low friction coatings**

NASA pioneered the use of vacuum-deposited thin film solid lubricants. They are of two types: the low –shear metal lubricants such as silver and lead and the laminar-shearing compound materials such as MoS<sub>2</sub>. The low-shear metal lubricants “creep” can be a problem. As a very thin film is needed for lubrication, the application of the lubricant film does not result in significant changes of dimensions. Low friction coating of metal-containing carbon (M-C) is used to reduce wear in mechanical contact applications.

### **1.3.12. Free standing structures**

Freestanding structures can be made by depositing on a surface (mandrel), then separating the coating on the mandrel surface or dissolving the mandrel. The technique is useful for fabricating very thin structures, complex surfaces, or foils or sheets of materials that are hard to deform by rolling. For example, beryllium windows used for X-ray transmission, boron thin-wall cones for high-frequency audio speakers. A relatively new application is the production of Micro Electro Mechanical System (MEMS) devices where very small structures are fabricated using deposition as well as etching processes.

### **1.3.13. Base coats for electroplating**

Materials that are difficult to deposit because of rapid oxide formation can have an adherent base coat applied by PVD processes and then the coating built-up by electro deposition. For example, plating on titanium, uranium and zirconium

where a base coat of a material like nickel or copper is applied by a PVD process before the electroplated coating is built up.

## **1.4. GENERAL METHODS FOR THE PREPARATION OF THIN FILM**

Physical vapour deposition (PVD) and chemical vapour deposition (CVD) are common methods for transferring material by atom-by-atom from one or more sources to the growth surface of a film being deposited onto a substrate. The deposition is normally carried out in a vacuum chamber to enable and control the composition. If the vapour is created by physical means without a chemical reaction, the process is classified as PVD. Many deposition methods have been developed in efforts to balance advantages and disadvantages of various strategies based on the requirements of purity, structural quality, the rate of growth, temperature constraints and other factors. The various methods used in the this films formation are discussed below;

### **1.4.1. Physical Vapour Deposition (PVD) Method**

There are various methods of physical vapour deposition such as thermal evaporation, electron beam evaporation, pulsed laser evaporation molecular beam epitaxy, ion plating, and activated reactive evaporation. The objective of these deposition process is to transfer atoms from a source to substrate, where film formation and growth follow automatically [4].

#### **1.4.1.1. Thermal evaporation**

In this method, thin films are prepared by the condensation of vapours produced by either evaporation or sublimation on the substrate. The most widely used thermal evaporation is simple and very convenient. Excellent and detailed reviews of the know-how of thermal evaporation are given by Holland [5].

Preparation of thin film by thermal evaporation is carried out in high vacuum to increase the mean free path of vapour atoms/ molecules, to avoid contamination and to get uniform films. Thermal evaporation may be achieved directly or indirectly by a variety of physical methods [6].

#### **1.4.1.2. Electron beam evaporation (EBE)**

In electron beam evaporation, an electron beam is accelerated through a potential of 5 to 10 kV and focused on the material. The electrons lose their kinetic energy mostly as heat and the temperature at the focused spot can become as high as 3000 °C. At this high temperature, most of the refractory metals and compounds can be evaporated. Since the temperature is high only at the focused spot, rest of the material will be cool. This results in lesser interaction between the material and the support, thereby reducing contamination. Since, the input power can be very high, extremely high rates of evaporation can be achieved even for high melting point materials [7].

#### **1.4.1.3. Pulsed laser evaporation**

Laser is a powerful tool in many applications especially in material processing. It possesses many unique properties such as narrow frequency band width, coherence and high power density. The light beam is intense enough to vaporize the hardest and most heat resistant materials. Besides, due to its high precision, reliability and spatial resolution, it is widely used in the industry to process materials like matching of the thin film, modification of materials, heat treatment, welding and micro patterning. The enormous intensity of a laser beam may be used to heat and vaporize materials by keeping the laser source outside the vacuum system and focusing the beam on the surface of the material to be evaporated. Using material in powder form can reduce degassing of the specimen [8].

#### **1.4.1.4. Molecular beam epitaxy (MBE)**

The molecular beam epitaxy produces epitaxial films by condensation of atoms. The depositions of single crystal (epitaxial) films are made by the condensation of one more beams of atoms or molecules from the source under vacuum conditions. The evaporation sources consist of a metallic chamber containing the evaporant with a small orifice. The orifice dimension is smaller than mean free path of the vapour in the chamber and the flow of molecules from the source is by effusion. The effusing molecular beam is precisely determined by the partial pressure of the vapour species within the chamber, and their molecular weight, source temperature and orifice dimension. The beam is directed onto the substrate by the orifice slits and shutters [9].

#### **1.4.1.5. Ion plating**

A combination of thermal evaporation onto a substrate which is simultaneously bombarded with positive ions from a glow discharge or an ion source is called ion plating. It refers to evaporate film deposition processes in which the substrate is exposed to a flux of high energy ions capable of causing appreciable sputtering before and during film formation. Since the system is a hybrid system provision must be made to sustain the plasma cause sputtering and heat the vapour source [10].

#### **1.4.1.6. Sputtering**

Sputtering was first discovered by Grove in 1852 [11]. When a solid or liquid is bombarded with atoms, ions, or molecules, several phenomena may arise, depending on the kinetic energy of the bombarding particles. At very low kinetic energy (<5eV), the interaction is confined to an outermost layer of the target material. Ions of noble atoms may be reflected on coming into thermal equilibrium

with the surface and evaporated. The potential energy of the species plays an important role because it is responsible for the ejection of secondary electrons or absorbed surface impurities or to the breaking of chemical bond.

When kinetic energy exceeds the binding energy of the atoms, atoms in the lattice are pushed into new position giving rise to surface migration and surface damage. When the energy approximately exceeds roughly  $4H$  ( $H$ -heat of sublimation of target material), the dislodging of atoms and their ejection to gas phase begins. This process is called physical sputtering. From a clean surface electron would need much higher kinetic energy (about 500 KeV for Co) to accomplish physical sputtering. For bombardment of surface under normal incidence more than one collision is necessary for the ejection of a sputtered atom because the momentum vector has to be changed by more than  $90^\circ$ . Only under oblique bombardment one can detect forward sputtering atom or ions which result from a single collision between an ion and a surface atom.

The ion bombardment of polycrystalline metal target was observed as early as 1912 and the results strongly suggested that the sputtering yield must be sensitive to crystal orientation. In 1955, a rather unexpected phenomenon relating to a single crystal sputtering was discovered by Wehner that the sputtered atoms are preferentially ejected in the close packed crystal direction. When a surface of a solid is bombarded with ions, several interactions of the ions with surface may happen;

1. The incident ions are reflected probably being neutralized in the process.
2. The impact of the ion causes the target to eject a secondary electron.
3. The ion impact causes some structural rearrangements in the target material.
4. The ion is buried in the target. This is known as ion implantation.

5. The ion impact sets a series of collisions in the target, possibly leading to the ejection of one of these atoms. Sputtering is the atom-by-atom deposition technique.

Sputtering is predominant in the energy region of incident electrons, 100 eV to 100 KeV. At higher energy region, the ion implantation becomes predominant [12, 13].

### **1.4.2. Chemical deposition method**

Chemical deposition techniques are most important method for the growth of films owing to their versatility for depositing a very large number of elements and compounds at relatively low temperatures. The various chemical deposition processes are discussed briefly as follows:

- Chemical vapour deposition
- Spray pyrolysis
- Electroless deposition
- Electrodeposition
- Screen printing
- Chemical bath deposition
- Spin coating
- Sol-gel method

#### **1.4.2.1. Chemical vapour deposition**

A simple definition of chemical vapour deposition is the condensation of a compound or compounds from the gas phase onto a substrate where reaction occurs to produce a solid deposit. The deposit material is formed by volatilization from either a liquid or a solid feed and is caused to flow either by a pressure differential or by the action of carrier gas to the substrate. The chemical reaction is

initiated at or near the substrate surface which produces the desired material in the form of a deposit on the substrate. The morphology, microstructure and adhesion of the deposit are strongly influenced by the nature of chemical reaction and the activation process [14].

#### **1.4.2.2. Spray pyrolysis**

Spray pyrolysis has been extensively used to deposit thin film oxides on large substrates. In principle, two types of experimental set ups are used to grow the oxides films [15, 16].

A) Conventional set up

B) Set up with preheat treatment

The conventional spray pyrolysis technique consists of spraying a diluted solution of appropriate substance from an atomizer into a heated substrate under normal atmospheric condition or controlled atmosphere. High pressure argon, nitrogen or air is usually used as spraying gas. The solutions are made by dissolving in suitable solvents such as ethanol, butyl acetate, propanol, hydrochloric acid or water.

In the arrangement with preheat treatments; a furnace to preheat the spray is placed between the atomizer and the substrate. The distance between the substrate and atomizer nozzle may be equal to or larger than about 20 cm and the typical gas flow rates are about 5 ml per min. To obtain more homogeneous films either rotating the substrate or rotating the sprayer is used.

#### **1.4.2.3. Electroless deposition**

This technique involves the reduction of metal ions to form the deposits but no external power supply is required to provide electrons. They are provided by a chemical reducing agent in the solution. Further a catalytic surface is used to initiate

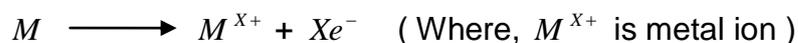
the deposition and then the metal itself must be catalytic for the deposition process. This enables to grow metal and alloy films on non-conducting substrates.

The principle is that the reacting anions and cations combine slowly and uniformly throughout the solution leading to the precipitation of hydrated oxides. Hard and well adherent films can be obtained by the post-heat treatment. Freezing agents like sodium citrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ ) and ammonia ( $\text{NH}_3$ ) are used to control the reaction. Silver ion is added as catalyst to improve adherence [17].

#### 1.4.2.4. Electrodeposition

Electrodeposition is a process of depositing a substance upon an electrode by electrolysis. The first application of the principle of electrolysis on the deposition of metal films is the subject of controversy but probably took place in 1838. The experimental arrangement requires a suitable electrolyte through which current is passed between two electrodes. The phenomenon of electrolysis is governed by Faraday's laws [18-21].

When a metal is dipped in a solution containing ions of that metal, a dynamic equilibrium between metal ion and metal. Metal ion gain an electron and get deposit at cathode and the metal atom goes into solution as metal ion with dissolved electron is set up. This is called metal / metal ion electrode,



The electrode gains an electron on itself, which attracts oppositely charged ions and water molecules holding them at the electrode/electrolyte interface by the electrostatic force. A double layer consisting of an inner layer interposed by preferentially adsorbed ions immediately on the electrode. It is followed by a second layer of charge opposite to that of the electrode surface and it is moved to stable position on it, release their ligands (water molecules) if solvated, release their

charges and the process undergo stimulated electro chemical reaction. The rapid depletion of the deposited ions from the double layer region is compensated by a continuous supply of fresh ions from the bulk of electrolyte. Semiconductors belonging to II-V group elements are mainly prepared by codeposition.

#### **1.4.2.5. Screen printing**

In the screen printing technique, the material in the form of paste is applied over the screen by a spatula. The substrate is placed at a short distance beneath the screen. The distance between the screen and the substrate is called the snap-off distance. A flexible wiper called “squeegee” is allowed to move across the surface of the screen, bringing it into contact with the substrate and forcing the paste through the open-mesh areas.

On removing the squeegee, the screen comes back to its original position due to its natural tension, leaving behind the printed paste on the substrate. Nylon and stainless steel are the commonly used mesh materials. To obtain uniformity in the transfer of paste through the screen, it is necessary to ensure that the printing edge of the squeegee is kept parallel to the screen throughout the printing step. Another important consideration is that the squeegee blade should be an inert material to the commonly used solvent. Generally neoprene polyurethane or polytetrafluoroethylene (PTFE) is used.

The squeegee pressure should be just sufficient to transfer the paste to the substrate. Excessive pressure causes irregular print edges and may permanently deform the screen over the edges of the substrate. The rheological characteristics of the paste namely, viscosity and surface tension strongly influences the quality of the print.

Thin prints result under the following conditions;

1. Low viscosity of the paste
2. Higher squeegee pressure
3. Small snap-off distance and
4. Hard squeegee blade.

Thick prints are obtained by the opposite conditions of the above parameters. Close control of the drying step is necessary before the sintering step [22].

#### **1.4.2.6. Chemical bath deposition (CBD)**

In CBD method, thin films are produced by immersion of the substrate in a liquid with tight control of the kinetics of formation of the solid. Most CBD reports in the literature concern sulfide and selenide thin film deposition. However, this technique has also been recently used for depositing metal oxide thin films. They can form the deposition of highly ordered and single crystalline array of nanostructures.

In CBD one or more metals in the form of salts,  $M^{n+}$ , and a complexing agent,  $L^-$ , in aqueous solution are used. The processes that occur in the CBD solution in general consist of the following steps:

1. Equilibrium between the complexing agent and water;
2. Formation/dissociation of ionic metal-ligand (ligands are the ions or molecules surrounding the metal ion) complexes
3. Hydrolysis and
4. Formation of the solid.

For instance, during the deposition of ZnO, the following reaction takes place:



The substrate  $\text{LiNbO}_3$  has inclined to  $64^\circ$  in XY plane. Initially a very thin ZnO seed layer was deposited using the laser pulsed deposition technique, and subsequently the substrate was submerged in hot alkaline solutions of  $\text{Zn}(\text{NO}_3)_2$ . The growth temperature and deposition time were  $70^\circ\text{C}$  and 60 min, respectively [23, 24].

#### **1.4.2.7. Spin coating**

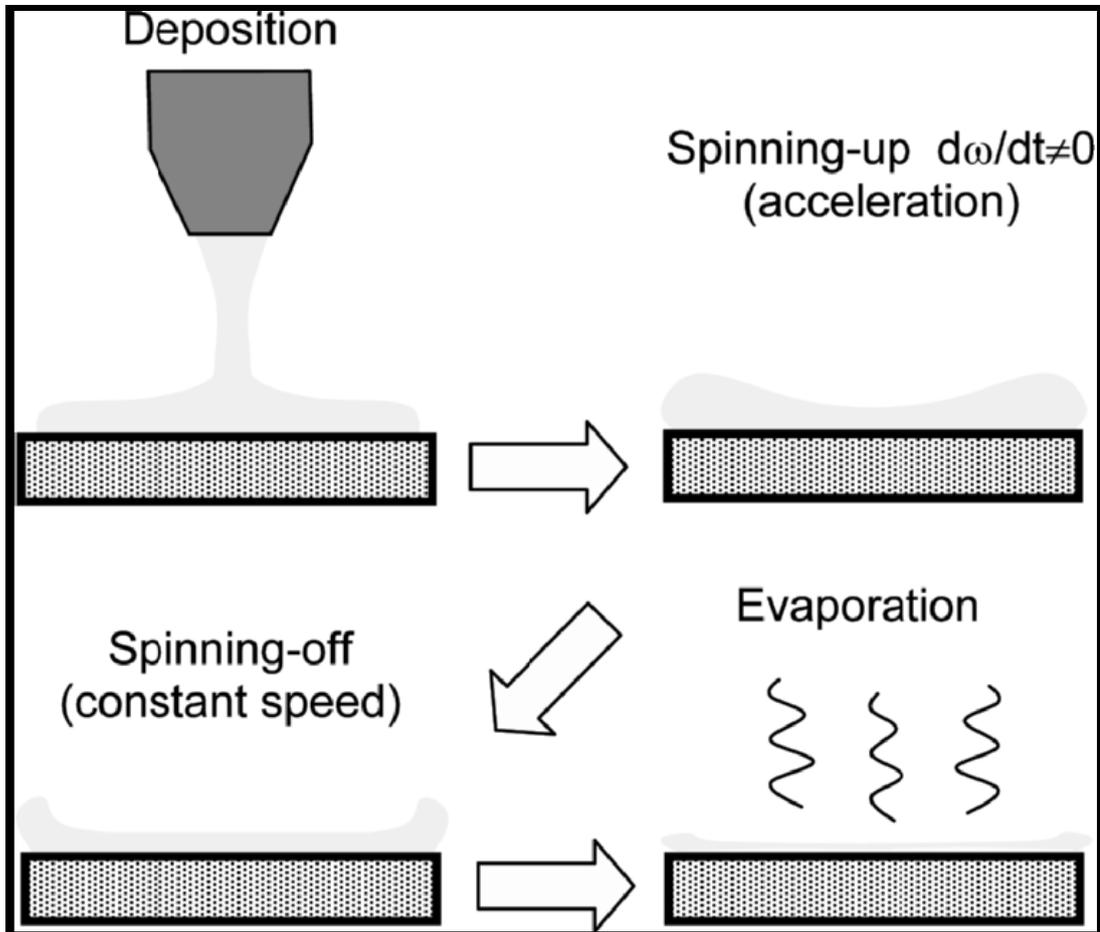
Spin coating is a well-established technology which is commonly used in the electronics industry. The uniformity and thickness of the film can be controlled by adjusting the rate and speed of spinning.

The spin coating process can be divided into the following four essential steps:

- (a) A small volume of liquid is placed on the surface;
- (b) The substrate is initially spun-up and the liquid flows radially outwards, driven by the centrifugal force.
- (c) While spinning, the excess liquid flows to the perimeter and leaves the surface as droplets. The thinner is the film, the larger is the resistance of flow.
- (d) The final stage is evaporation, which is the primary mechanism of solidification.

A summary of the spin-coating process is shown in Fig.1.4. The process of spinning is a reliable method for the deposition of thin films because the liquid tends towards a uniform thickness during spin-off. The film thickness tends to remain uniform, provided that the viscosity of the solvent is not shear dependent and does not vary across the substrate. In order to minimize contamination, the spin coating should be carried out in a clean environment. The substrates are mounted on a spinning stage and held in place with suction. Following the spin coating step, the substrates are placed in an annealing furnace to remove the solvent. Annealing is a heat treatment process in which a material is subjected to elevated temperature for

an extended time and then slowly cooled down. Both the heating and cooling are carried out in a controlled manner [25-28].



**Fig.1.4 Spin coating process**

#### **1.4.2.8. Sol-gel**

Sol-gel is a colloidal suspension that can be gelled to form a solid. Although in the existence since the early 19th century, the sol-gel process gained popularity only in the 1950s. Since the process has been employed to fabricate films for a vast number of industries, with applications in optics, electronics and of course sensors. Using the sol-gel process, it is possible to fabricate ceramic or glass materials in a wide variety of forms: ultra-fine or spherical shaped powders, thin film coatings,

ceramic fibers, micro/nano-porous inorganic membranes, monolithic ceramics and glasses, or extremely porous aerogel materials.

In general, the sol-gel process involves the transition of a system from a liquid “sol” (mostly colloidal) into a solid “gel” phase. The precursors for synthesizing these colloids consist of metal or metalloid elements surrounded by reactive ligands. Metal alkoxides (an alkoxide is the conjugate base of an alcohol and therefore has an organic group bonded to a negatively charged oxygen atom) are popular precursors because they react readily with water. The most widely used metal alkoxides are the alkoxy silanes such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS). However, other alkoxides such as aluminates, titanates, and borates are also commonly used in the sol-gel process.

The precursor is subjected to a series of hydrolysis and polymerization reactions which lead to the formation of a new phase of colloidal suspension. A series of standard sol-gel reactions for organometallic precursors are shown below:



Where, M is the metal and R is an alkyl group. Once the sol is cast into a mould, the colloidal particles condense into a new phase, gel, in which a solid macromolecule is immersed in a liquid phase (solvent).

It is possible to produce thin films on a substrate by using methods such as spin coating, dip-coating, and drop casting. With further drying and heat treatment, the gel is converted into dense ceramic or glass. If the liquid in a wet gel is removed under a supercritical condition, a highly porous and extremely low-density material

called an aerogel is obtained. The viscosity of a sol can be adjusted to a desired viscosity range to obtain ceramic fibers. Ultra-fine and uniform ceramic powders can also be formed by precipitation, spray pyrolysis, and emulsion techniques. After the formation of the sol-gel film, it is generally annealed. In order to prepare high quality thin films, it is of paramount importance to control the annealing parameters. Annealing is carried out to convert the organometallic film to a metal oxide in addition to enabling and controlling crystallization and grain growth. It also serves to remove organic compound, which usually evaporate off the film at elevated temperatures. Furthermore, it promotes adhesion to the substrate. Unlike many other fabrication methods, which require starting materials to have the same composition as the final product, sol-gel offers an economically feasible avenue to explore different ratios and combinations of the compounds. The sol-gel method can be employed to form nanostructured thin films for sensing applications and the grain size of these thin films can be engineered for the right application. For example, Nanostructured indium was prepared by using ethanolic solutions of an indium isopropoxide precursor. The solutions were spin coated on sapphire substrates and annealed at 500 °C for 1 h in ambient air. This resulted in a well-developed polycrystalline and highly porous microstructure composed of approximately spherical grains with an average size of approximately 20 nm [27, 28].

## **1.5. THEORETICAL ASPECTS OF VARIOUS STUDIES**

### **1.5.1. Structural studies**

Thin films assumed with increasingly complex structures in view of their applications, which demand tailor-made properties. As a result, sophisticated characterization techniques have emerged to understand the multifaceted properties

of thin films. X-ray diffraction is treated as the best method for estimating crystallographic parameters. The diffraction peaks were identified by using ASTM in order to study the crystalline nature and structure of the films. X-ray diffraction studies were carried out using a JEOL (JDZ8030) X-ray diffractometer with Cu $\alpha$  K $\alpha$  radiation. The lattice parameters 'a' and 'c' for the hexagonal structure were calculated using the formula;

$$d^2 = \frac{1}{4}(h^2 + k^2 + hk) / 3 a^2 + l^2 / C^2 \quad \dots \quad 1$$

Where, h,k,l represent the lattice planes and 'd' is the interplanar distance. In the case of cubic structure, the lattice parameter 'a' is estimated by using the following relation;

$$d^2 = a^2 / (h^2 + k^2 + l^2) \quad \dots \quad 2$$

Where h,k and l represent the lattice planes. The observed 'd' values are compared with ASTM index to determine the crystal structure.

The grain size (L) of the films is estimated from the Debye-Scherrer formula;

$$L = 0.9 \lambda / \beta \cos \theta \quad \dots \quad 3$$

Where,  $\lambda = 0.1542$  nm,  $\beta$  is the full width at half maximum (FWHM) and  $\theta$  is the Bragg angle.

The preferred orientation of the crystalline thin films and the degree of crystalline order are determined by the following equations; the degree of preferred orientation,  $F_{hko}$  along (hko) axis is known as (hko) axis orientation and given by the expression;

$$F_{(hko)} = \frac{\sum(hko)I(hko) / I(ohko)}{\sum(hkl)I(hkl) / I(ohkl)} \quad \text{and} \quad \dots \quad 4$$

The degree of crystallize order  $G = \sum (hkl)I(hkl)I(ohkl) / d \quad \dots \quad 5$

Where,  $I_{(hkl)}$  is the intensity of the (hkl) line for films and  $I_{(hkl)}$  is the intensity of the (hkl) line for the randomly oriented powder sample according to ASTM data and 'd' is the thickness of the film [29].

### 1.5.2. Optical Absorption Studies

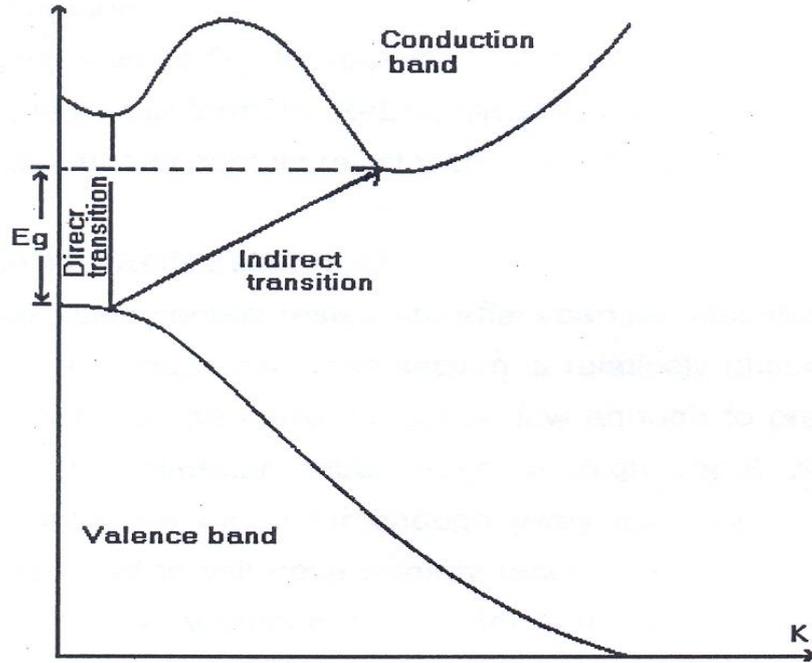
Optical absorption in solid results mainly due to one of the following processes:

- 1) Excitation of crystal vibration
- 2) Formation of excitons
- 3) Excitation of free electrons and holes within allowed bands
- 4) Excitation of free electrons and holes from one band to another of the same type of band
- 5) Excitation of electrons across the gap from the valence band to conduction band
- 6) Excitation of electrons across the gap from the valence band to imperfection level
- 7) Excitation of an electron from an imperfection to the conduction band.

Among these, last three absorption processes give rise directly to photoconductivity excitation across the gap. The absorption of radiation gives rise to transition of electrons between the valence and conduction bands is of two types (Fig.1.5);

#### (a) Direct transition

The necessary condition for a direct transition to take place is that in the excitation process the electrons that occur has no change in the expected K value. The absorption coefficient for direct transition is usually in the order  $10^4 - 10^5 \text{ cm}^{-1}$ . The following dependences are observed during this transition.



**Fig.1.5 Direct and indirect transitions in valence and conduction bands**

$$\alpha \propto (E_v - E_i)^{1/2} \text{ for allowed transitions}$$

$$\alpha \propto (E_v - E_i)^{3/2} \text{ for forbidden transitions}$$

Where  $\alpha$  is the absorption coefficient,  $E_v$  is the energy of the top of the valence band and  $E_i$  is the energy of the initial state from which the transition is made. If  $\alpha^2$  is plotted against photon energy, a straight line is obtained which cuts the energy axis with an intercept equal to the band gap.

**(b) Indirect transition**

The transitions involving a change in the crystal momentum ( $k \neq 0$ ) are termed as indirect transitions. In this case, absorption of both a photon and the absorption of a photon and the emission of photon take place. The absorption coefficient is usually in the order of  $10^1 - 10^3 \text{ cm}^{-1}$ . The following dependences are observed during indirect excitation;

$$\alpha \propto (E_p - E_G)^2 \quad \text{if allowed direct transition at } k=0$$

$$\alpha \propto (E_p - E_G)^3 \quad \text{if forbidden direct transition at } k=0$$

If  $\alpha^2$  plotted against photon energy, a straight line is obtained; the intercept on energy axis gives the band gap for indirect transitions [30].

### 1.5.3. Resistivity measurements

Resistivity measurements of semiconductor materials are geometry dependent on the boundary conditions. Most semiconducting materials have high temperature coefficient of resistivity. For precise measurements, corrections should be made. Temperature coefficient of resistivity changes appreciably with impurity concentration. The oldest way of finding resistivity is by direct measurement using a rectangle sample by the formula,  $R=L/A$ . Disadvantage of this method is that it will have the influence of contact resistance [31]. This contact resistance effect can be minimized in a two point probe method if the specimen cross section is relatively uniform. It should be noted that in this case, the current must be low enough to prevent heating of the sample. The voltmeter must have high input impedance and measurements must be made far enough away from the contacts that any minority will have already recombined. The requirements for the contacts are not very stringent and vary from plating or solder to spring loaded mesh. If the contacts are very poor the equi-potential lines will be distorted near the ends. To reduce this effect, the maximum cross sectional dimension should not be more than one third of the length of the sample. Because of poor contacts, errors may be introduced when the current enters and leaves the corners. This is the latest two probe instruments to measure the crystal diameter using resistivity measurements [32].

#### **1.5.4. Morphological Studies**

In order to study the morphology of a semiconductor film, simple reflection modes of the optical microscope can be extended. But these techniques are limited in spatial resolution to a few of a micrometer. The extension of the resolution is allowed in electron beam techniques. The most versatile among these is a scanning electron microscopy (SEM). The convenience of conventional scanning electron microscopy is partly due to the long working distance between the final lens and the sample surface and partly due to the ability to study directly almost any free surface. SEM offers several modes of operation. The most widely employed is secondary electron imaging, which gives images of better than 100 Å resolution.

The SEM studies carried out to study the morphology of the deposited films. The SEM photographs provide the nature of the surface. i.e. uniformity, smoothness and cracks, the nature of the grains, i.e. shape, particulate or interconnected and grain size. In the present work, surface morphological studies were carried out using a JEOL (JSM 35) - Scanning electron microscope [33].

### **1.6. GENERAL PROPERTIES OF SOME METAL OXIDES**

The properties of metal oxides such as ZnO, Cu<sub>2</sub>O, SnO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> used in the present investigation are summarized as follows;

#### **1.6.1. Zinc oxide**

The ZnO is formed on burning the metals in air or by pyrolysis of the carbonates or nitrates. ZnO is normally white turns yellow on heating depending on its thermal history. It is a n-type semiconductor because of non-stoichiometry due to metal abundance and impurities. It crystallizes wurtzite structure, where in the Zn<sup>2+</sup> ion is occupied in tetrahedral holes. Both Zn and oxygen atoms have four tetrahedral

nearest neighbors surrounded by four oxygen ions. It belongs to n-type semiconductor containing excess of interstitial metal atoms. Its composition is  $M_{1+x}Y$ . (Table 1.1)

**Table 1.1 General properties of zinc oxide**

<b>Formula</b>	<b>ZnO [Zinc (II) oxide]</b>
Physical state	Crystalline as well as amorphous
Colour	White
Molecular weight	81.4084
Melting point	2248 K
Decomposition temperature	895 °C
Specific gravity	5. 606 gm/cm <sup>3</sup>
Structure	Wurtzite ( Hexagonal )
Solubility in water	Insoluble
Corrosivity	Non-Corrosive in presence of glass
Flammability	Non-Flammable
Magnetic property	Paramagnetic
Stability	Stable

### 1.6.2. Cuprous oxide

The two forms of copper oxides are CuO and Cu<sub>2</sub>O. The Cu<sub>2</sub>O is a brownish-red solid and found as mineral. When copper is exposed to air, it will naturally oxidizes to copper (I) oxide. It may be obtained when copper is subjected to high temperature and high oxygen pressure. Cu<sub>2</sub>O has the typical primitive cubic

structure. In the cuprous oxide, positive hole in a metal ion is effective migrating unit and the type of conductivity is p-type semiconductor. The energy gap for this type of semiconductor corresponds to the energy required to move of a cation vacancy from where it is electrostatically held (Table 1.2).

**Table 1.2 General properties of Cuprous oxide**

Formula	Cu <sub>2</sub> O [ Copper (I) oxide, or Cuprous oxide]
Physical state	Crystalline powder
Colour	Reddish brown
Molecular weight	240.80
Melting point	1508 K
Decomposition temperature	20273 K
Specific gravity	6.0 gm/cm <sup>3</sup>
Structure	Simple cubic
Solubility in water	Insoluble
Corrosivity	Non-Corrosive in presence of glass
Flammability	Non-Flammable
Magnetic property	Paramagnetic
Stability	Stable

### 1.6.3. Tin oxide

The addition of aqueous ammonia to Sn<sup>2+</sup> solution gives the white hydrous oxide which is dehydrated to black SnO when heated in suspension at 60 to 70 °C. It disproportionates above 250 °C to give Sn and Sn<sub>3</sub>O<sub>4</sub> and above 500 °C to give Sn and SnO<sub>2</sub> (Table 1.3).

**Table 1.3 General properties of Tin (IV) oxide**

Formula	SnO <sub>2</sub> [Tin (IV) oxide ]
Physical state	Crystalline powder
Colour	White
Molecular weight	141.00
Melting point	1903 K
Decomposition temperature	895 °C
Structure	6.95 gm/cm <sup>3</sup>
Solubility in water	Insoluble
Corrosivity	Non-corrosive in presence of glass
Flammability	Non-flammable
Magnetic property	Paramagnetic
Stability	Stable

#### 1.6.4. Cobalt (III) oxide

The two main cobalt oxides are CoO and Co<sub>3</sub>O<sub>4</sub> and CoO is olive green in colour which can be prepared by reaction of the metal with oxygen at high temperature. It has a rock-salt structure and it is anti-ferromagnetic at ordinary temperature. When cobaltous oxide is heated at temperatures between 300 – 500 °C in oxygen, the Co<sub>3</sub>O<sub>4</sub> is readily obtained. At room temperature and up to ~900 °C, Co<sub>3</sub>O<sub>4</sub> is thermodynamically stable form. Co<sub>3</sub>O<sub>4</sub> has the typical spinel structure and shows magnetic attraction (Table 1.4).

**Table 1.4 General properties of cobalt (III) oxide**

<b>Formula</b>	<b>Co<sub>3</sub>O<sub>4</sub> [ Tricobalt tetraoxide ]</b>
Physical state	Crystalline powder
Colour	Black – grey
Molecular weight	240.80
Melting point	895 °C
Decomposition temperature	895 °C
Specific gravity	6.2 gm/cm <sup>3</sup>
Structure	Face centered cubic
Solubility in water	Insoluble
Corrosivity	Non-corrosive in presence of glass
Flammability	Non-flammable
Magnetic property	Paramagnetic
Stability	Stable

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