CHAPTER I

General Introduction

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1.1 Solid thin films

An ideal thin solid film can mathematically be defined as a homogenous solid material contained between two parallel planes and extended infinitely in two directions (x,y) but restricted along the third direction (z), which is perpendicular to the x-y plane /1/. It is formed by atom by atom or molecule by molecule condensation process. The dimension of such solid film along z-direction, known as thickness of the film, in general, is of the order of microns or less i.e. much less than those along other two directions. As the thin films are very thin layers of solid materials, they cannot support themselves. Therefore they are generally grown on suitable supports known as substrates.

If the thickness of a solid film is comparable to or less than the mean free path of electrical conduction process, diffusion length, effective de-Broglie wavelength etc then thickness plays the key role on different electrical as well as optical processes like electrical conductivity, optical absorption etc. If the thickness of the films is of this order the charge carriers invariably suffer surface collisions and thus surface scattering of carriers becomes a predominant factor. All the physical properties of a thin film are, in turn, related to the method of preparation and the growth parameters like environmental conditions, substrate temperature, source temperature, angle and rate of deposition, degree of vacuum etc of the growth environment. The thin film properties are also very sensitive to the structural nature of the films. The structure sensitive attributes are strong function of the particular growing method as well as the deposition environment and subsequent treatment to the prepared films.

A real film, however, deviates considerably from the ideal one since its two thickness limiting surfaces are never exactly parallel when formed in the best experimental deposition conditions and also the material contained between the two surfaces are neither strictly homogenous nor uniformly distributed. It is also a true that such a film also contains many imperfections and discontinuities which contributes immensely in deviating from the ideal properties of the film.

1.2 Characteristics of solid thin films

All solid thin films irrespective of their deposition techniques are invariably associated with native defects like lattice disorder, stacking faults, twinning, dislocations, grain boundary defects etc. which influence the electrical, optical as well as the mechanical properties of the films. Surface state of films also has a dominating role in wide scale modification of the optoelectronic properties. The surface atoms are usually under the influence of unbalanced forces and in the unsatisfied vacancy condition. So the absorption of gases on the thin film surface and solid state reactions are often observed in thin films rather than in bulk materials.

The properties of a thin film may be largely altered up to some desired level by incorporating some controlled amount of suitable impurity /2,3/ which results in acceptor or donor levels in the forbidden gap. The positions of these donor or acceptor levels actually depend on the valence state of the substituted impurity atoms. Various native defects /4,5/ also cause some irregularities in the average potential in a solid which lead to the formation of new discrete energy levels in the forbidden gap. In the photoconductivity processes, the imperfections play a significant role. They either act as trapping or recombination centers for the carriers.

Trapping is a fundamental process for energy storage in the material which acts as positive potential center for electrons and localized negative potential centers for holes. The degree of localization determines the depth of the energy level. The activation energy of a shallow level is of the order of kT or less at room temperature and much more than kT for a deep level /6/. Depending on the trap depth, energy of carriers and temperature, electrons remains in a trap for about 10^{-8} sec to hours or days. A recombination center have a greater probability of recombination with carriers of opposite sign than of being re-excited to the free states and lie near the middle of the forbidden gap. A recombination center at one condition of light level and temperature may act as a trap at another condition of light level and temperature or may become bleached /7/. The occupancy of trapping center is determined by thermal equilibrium process and the occupancy of recombination centers is determined by the kinetic process of recombination. Measure of trapping centers may be made from the photoconductivity growth and decay /8-11/,

thermally stimulated current /12-14/, optically stimulated traps emptying process /15/, space charge limited currents /16,17/ etc.

1.3 Some physical attributes of II-VI solid thin films

The II-VI group of semiconductor compounds includes sulphides, selenides, tellurides and oxides of Zn, Cd & Hg. This group of compounds has a wide variation of bandgap. For example HgTe has an intrinsic band gap of ~10^{-2} eV whereas ZnO & ZnS have a band gap of greater than 3eV. Because of this wide variation of band gap electrical properties of this group of semiconductors range from near insulator to semimetallic behaviour /18-23/ and each individual member of this group distinctly possesses different photoresponse characteristics. Also photo conductors of them may be used over a wide spectrum of application covering the electromagnetic radiation from near UV to near IR region. Most of the II-VI compounds are crystalline in Zincbland structure expects a stable phase of HgS which has hexagonal structure. ZnS, CdTe, CdSe & CdS may be crystalline in both Zincblend & Werizite forms whereas ZnTe is crystalline in Zincblend form only.

So far as technological aspects are concerned II-VI group of compounds has surpassed the more ionic I-VII insulator and more covalent III-V semiconductor in the field of material research as well as applications. The II-VI semiconductor compounds usually possess high resistively (~ 10^3-10^6 Ωm), which is a prerequisite condition for good photosensitivity. Bulks as well as thin films form of these materials are usually polycrystalline and the crystallinity controls the photosensitivity.

Vacuum deposited thin films of II-VI compounds at room temperature substrates processes fine grained of amorphous type structures and low electrical resistively. Films with higher grain size and improved electrical conductivities may be obtained by deposition of films at elevated substrate temperatures and proper subsequent thermal annealing, which effectively reduces perturbations on the grain boundaries. II-VI semiconductors both in bulk and thin film forms are highly photosensitive. This may be further ignited by incorporation of donor or acceptor impurities, although the imperfection levels due to certain native defects formed during the growth process itself

effectively thus the same. Also due to variation from the stoichiometry II-VI films may be itself considered as the self doped films.

Photoelectronic properties particularly of compounds like CdTe, CdSe, CdS, ZnTe & ZnS in the form of thin film is of considerable interest because of having potential applications is different devices like low cost solar cells, photochemical cells, different photo detectors, phototransistor, X-ray detectors, phase memory devices etc. Also ternary compounds of such materials have been the subject of wide investigations /24-26/. The bandgap of ternary compound films may be varied with growth conditions like composition, substrate temperature, residual pressure etc.

Among the semiconductor of II-VI group CdTe and CdSe films are used in the fabrication of gunn oscillators, injection lasers and electrography. In solar cell technology, which is not based on Si and Ge, II-VI compounds play an important role /27-30/. CdTe exhibits both n-type and p-type conductivity which permits its utilization as solar cells in both homojunction and heterojuntion configuration. It also possess the largest atomic number in the II-VI compound series and gives good absorption characteristics so that in theoretical considerations a nearly ideal solar cell with highest theoretical efficiency may be constructed. CdS is referred as a model semiconductor and study of its optical constant in the sub-band gap region is important so far as the use of this material in optical devices are considered. It may be noted that depending upon various growth conditions, compounds like CdTe and ZnTe may exhibits both n-type and p-type conductivity.

PN homojunction may be prepared both from CdTe and ZnTe. Polycrystalline ZnTe films are generally used in a tandem solar cell structure and in the fabrication of quantum well structure. The higher bandgap of ZnSe enhances the blue response and increases the open circuit volt of the solar cells. ZnTe has potential applications as window materials, blue green laser diodes, light emitting diodes, dielectric mirrors, filters etc.

The CdSe thin films are very sensitive to oxygen impurities. So the deposition of stable photosensitive CdSe films is a matter of considerable interest. These films have pronounced annealing as well as ageing effects. The CdSe thin films have been successfully utilized in thin film transistor operations /31,32/. All cadmimum

chalcogenide films are widely used in fabrication of solar cells, thin film transistors, γ ray detectors, IR detectors, photochemical cells, switching diodes, electro-optic modulators, photoconductors, space charge limited diodes etc.

1.4 Optoelectronic importance of solid thin films

Semiconductor devices are basically used for the conversion of electric signal to optical signals and vice versa. Solid thin film has diverse field of applications like electronic industries, solar energy utilization, space science, high memory computer elements, different type of sensors etc /33-37/. Because of that physics of optoelectronics based on solid thin film has itself immersed as an important field of study and research. What is important for a substance in thin film form is that some of its properties like electrical transport differ entirely from their bulk ones. Again different physical and chemical, structural properties of thin films vary widely with their different growing conditions. However the acquired capability of controlling properties of the thin film by altering its growth conditions is very important so far as electronic, optoelectronic and device applications of thin films are concerned. Wide variety of scientific, engineering and industrial applications has raised the demand for better scientific study and understanding of the dependence of various properties of thin film on different physical parameters.

Presently thin film based devices like monolithic and hybrid circuits /38-40/, field effect transistors and various sensors have been developed for different applications like switching devices, high density memory system for computer hardware circuit etc. Thin films play a significant role in the field of microelectronics, optical coating, integrated optics, quantum engineering, informatics, solar energy conversion devices, metallurgical coating, surface engineering etc. In micro-electronics materials deposited in the form of films are widely used for fabrication of integrated circuit (IC) /41,42/, large scale integration (LSI) /43/ and very large scale integration (VLSI) /44/ etc. IC, using thin film of II-VI semiconductor, has also been properly fabricated /45/. Production of LSI with 10^4 chips and VLSI with 10^6 chips have opened new possibilities of microminimization with the use of thin film. These types of technological advancements in the thin film

circuitry are sure to play an increasing important role in different technological applications of present days.

In the field of optics, thin films are used in the preparation of anti-reflection coating, reflection increasing coating, interference filters etc /46,47/. Optoelectronic devices /48-56/ are essential in the fiber-optics communication, image processing, radiation detectors, remote acting devices etc. These are particularly based on the photoresponse properties of thin films. In devices like photodiodes, laser diodes, IR detectors, solar cells, photochemical cells, photolumincescenee devices etc photoresponse properties of thin film are successfully utilized. Using photosensitive thin film, radiation detectors from far IR region to high energy nuclear particles, are properly fabricated. These are also used in light sensitive switches, conversion of light energy to electrical energy, contact less remote acting devices etc. In optoelectronics, use of thin film photoresistors as active photosensitive device, are increasingly popular /57,58/. Other applications of thin film are electro luminescent displays /59/, bio-medical devices /60/, gas detectors /61/, television photophosphar /62/, micromagnetics, micro metallurgy, high TC super conductors etc. Significant advances in material preparation technique have led to different type of binary and ternary semiconductor compounds. The availability of large number of such compounds, with wide variety of different and often unique properties, enables the optimum materials to be selected for significant practical application as well as theoretical work.

Thin films are also of great help for obtaining information regarding many basic properties of solids. It may be noted that many of the fundamental solid properties in thin film differ considerably from those of bulk materials and sometimes new phenomenon are observed in the thin film state. The large surface to volume ratio, higher packing fraction, geometrical and quantum size effects are some of the specific characteristics which can be effectively achieved in thin films. For these purposes the thin films of metals, semi conductors, dielectrics, inorganic and organic materials are prepared by using various techniques specific to their needs, and along with the structural investigations, various properties of the films are studied under different ambient conditions. Such study has now a days tremendous technological importance so far as the different device base applications are concerned.

1.5 The processes of film growth

In thermodynamically stable films all atoms or molecules should be in there minimum potential energy sites and any new atom or molecule, takes the position and orientation, energetically compatible with the neighboring atoms of the substrate or previously deposited layer. Hence the occupation sites of freshly arrived atom or molecule is determined energetically both by substrate and the previously deposited layer. When the vapour atoms strike the substrate surface, they interact with the surface atoms via Van-der-Waals forces and get physically absorbed. These absorbed atoms soon loose the velocity component normal to the surface, but still retain the velocity component in the plane of the substrate.

They execute a random walk motion and move over the surface of the substrate from one potential well to another due to inherent kinetic energy. In course of the random walk there occurs several encounters with the already absorbed atoms and during this migration process; they combine to form nuclei or clusters. This process of addition, absorption, migration results in formation of critical nuclei and stable cluster, which is called nucleation. The impinging atoms may also be desorbed after a stay of finite time. Under the appropriate conditions, when the rate of adsorption becomes greater than the rate of desorption the small clusters of absorbed atoms begin to enlarge, leading to stable nucleation /63/.

The process of nucleation yields three-dimensional randomly distributed islands, with their height much less than the lateral dimension, which grow further by the addition of newer atoms from the vapour phase as well as by diffusion. The formation of the islands and their growth is called the island structure stage. The growing islands coalesce into one another by surface and volume diffusion forming a network structure in which the deposited material is separated by long, irregular and narrow channels. The coalescence is too short and involves considerable transfer of mass among islands by diffusion. As deposition advances, the secondary nucleation occurs in these channels and thus a continuous film with optimum thickness is formed, when these channels are bridged together. The optimum thickness for continuous stage is also dependent on the nature of deposits, mode of deposition, different parameters etc

The vapourization of multicomponent alloys or compounds is usually accompanied by dissociation of both. The components may evaporate at different rates because of their different vapour pressures and for their different tendencies to react with the supporting material thereby producing non stochiometric films. By using inert support material, suitable evaporation temperature, a large number of alloys and compounds can actually be deposited with only slight deviation from the original composition /64/.

II-VI compound films can be deposited with proper stochiometry by keeping the substrate temperature at some suitable value /65/. Too low temperature of the substrate prevents a uniform distribution of the atoms being absorbed. Too high temperature of the substrate causes the atoms that just arrived, to re-evaporate and leave the substrate. Therefore an optimum substrate temperature is desired in thermal evaporation to grow good quality solid thin films in which stochiometric compositions are maintained.

1.6 Deposition of solid thin films

1.6.1 Different methods of deposition

From variety of metals, semiconductors, alloy or insulators thin films are successfully prepared by using different deposition techniques. In general, different methods of thin film preparation may be mainly divided into four groups.

(i) Physical vapour deposition (PVD)

(ii) Sputtering

(iii) Chemical vapour deposition (CVD)

(iv) Chemical deposition.

PVD method may be used for the deposition of metal alloy and many compound films, where the material evaporates or sublimates in high vacuum due to thermal energy and the vapour stream of atoms or molecules condense on the substrate in order to form a continuous film of required thickness /66-68/. High vacuum is a primary requirement of this method. Physical vapour deposition may be obtained by variety of methods like thermal evaporation, flash evaporation, molecular beam epitaxy, activated reactive evaporation, laser evaporation etc. As the source of heating, refractory materials like tungsten, tantalum or molybdenum in the form of wire or strip of different shapes are generally used. The choice of these mainly depends on the materials to be evaporated.

Different methods of sputtering are there, which are glow discharge sputtering, low pressure sputtering, reactive sputtering, rf sputtering, magnetron sputtering, triode sputtering etc /69-71/. High vacuum is a primary requirement of this method also. In sputtering target surface (cathode) is bombarded by energetic particles, which cause ejection of surface atoms. Atoms can also be ejected from the surface of cathode by impinging energetic positive ions of noble gases at reduced pressure under high d.c. voltage. Ejected atoms then get condensed on a substrate (anode) to form a film.

The deposition of thin film from gaseous phases by thermal decomposition or chemical reactions on substrate surface at high temperature is known as the CVD process or vapour plating. The rate of reaction in the process may be controlled by introduction of carrier gas in the system. CVD process is achieved by variety of technique viz thermal deposition, vapour phase reaction, vapour transportation method etc /72,73/. Thin film of inorganic and organic compounds are generally fabricated by these processes.

In chemical deposition method, thin films are deposited on the substrate from aqueous solution either by passing a current or by chemical reaction under appropriate conditions. Electro deposition, electroless plating deposition by chemical reaction, anode oxidation etc are different techniques used under chemical deposition for preparation of films and are generally used for the deposition of thick metallic or alloy films /74/. For these two methods; CVD and chemical deposition, a high vacuum is not an essential condition.

In all these deposition techniques, three primary events are involved /75/, which are

(i) creation of substances to be deposited in an atomic, molecular or particular form prior to deposition.

(ii) transportation of substances in the form of vapour stream or spray.

(iii) formation of films on the substrate by the nucleation and growth process.

1.6.2 Selection of the process of deposition

Although there are various processes of deposition one must select the appropriate process of deposition, according to the requirements. An ideal process of deposition should have the following characteristics (a) capability for the deposition of any material

metal, alloy, chemical compounds etc. (b) ability to form crystalline or amorphous deposits (c) retention of the stochiometric composition (d) good adhesion to different substrates (e) variability of residual stress and defect concentration (f) ability for deposition over wide range of various deposition parameters (g) ability for variation of wide range of micro-structural parameters (h) good throwing power (i) ability to control the film thickness.

There is no single process to satisfy all these requirements. Each process carries its own advantages or disadvantages. It is the requirements of the application process itself, that determines the choice of deposition techniques. Some of the general criteria for this selection are (a) materials to be deposited (b) required nature of films (c) substrate limitations and properties (d) substrate bombardment and subsequent morphological effect (e) throwing power and rate of deposition (f) availability of required apparatus and (g) cost of different items.

Thermal evaporation techniques satisfy most of the above criteria. Although during thermal evaporation the growth process occurs far from thermodynamic equilibrium, still due to its simplicity and versatility of vacuum evaporation, it is very advantageous to obtain materials particularly in the fabrication of devices on insulating substrates /76/.

It is used extensively for preparation of thin layers of photoconductors /77/. For preparation of semiconductor films, particularly II-VI compound semiconductor, vacuum methods making use of evaporation and sputtering, continue to receive support from workers interested in the field of research of basic physical properties and also in the fabrication of numerous devices for different branches of science and technology /78-81/.The process of sputtering is carried out at some higher pressure than vacuum evaporation and so there is a possibility of contamination of film by the existing gases. So for preparation of quality controlled thin films, vacuum evaporation technique is the best so far as the degree of vacuum is concerned.

The present work is mainly devoted to the study of the proposed physical properties of thin film of CdSe deposited in vacuum on to glass substrate held at different substrate temperature by the thermal evaporation technique.

1.6.3 Thermal evaporation technique

During thermal evaporation materials are transformed into vapour from by means of resistive or RF induction heating. During heating when some surface atoms acquire thermal energy sufficient to break bonds with other surface atoms then they leave the surface as vapour. The heat of vapourization (ΔH_v) is the energy that removes the atoms from the bulk substance. Atoms after leaving the parent material possess only kinetic energy which on average is 1.5 kT (= 0.2 eV) per atom and this equals to a small fraction of total heat of vapourization, where T is the ambient temperature inside the vacuum chamber. The major part of the heat of vapourization is spent to overcome the attraction between atoms in the bulk materials.

Since vapour obeys ideal gas law at low pressure and ΔH_v varies only slightly with temperature (i.e. approximately constant), the vapors pressure P_v can be expressed from Clapeyron-Clausius equation as

$$\ln P_v = \text{Const} - (\Delta H_v / RT) \qquad (1.1)$$

where R is the gas constant. When the evaporating molecules are immediately removed so that none return to parent material, the rate of evaporation is given by Langmuir expression

$$G = C\, P_v (M/T)^{1/2} \qquad (1.2)$$

where M is the molecular weight and C is a constant. The evaporation rate is lowered by the contaminants present on the evaporant. Estimation of vapour pressure of materials at high temperature is usually made from evaporation rate. To achieve reasonable evaporation rate, the evaporation is to be typically carried out by heating the material to be evaporated until its vapors pressure is 1.33 Pa (10^{-2} torr). Combining (1.1) and (1.2), the rate of change of evaporation rate with temperature change can be estimated by

$$dG/G = \{(2.303B/T) - (1/2)\} dT/T \qquad (1.3)$$

where $$B = (\Delta H_v)/(2.303.R)$$

In case of metals 2.303 B/T is in the range of 20 to 30 which indicates large change in evaporation rate for small change in temperature /82/. Thus to achieve desired

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evaporation rate, accurate temperature control is necessary. In conventional vapour deposition, the vapourised atoms obey Boltzmann distribution of thermal energies (0.01 – 1eV) with most atoms reaching the substrate with energies less than 0.20eV. The structure and properties of vacuum deposited films are mainly governed by the available energy per condensing atom.

In case of thermal evaporation of multicomponent alloys or compounds the components may evaporate at different rates with different vapour pressures. If a binary alloy is to be volatilized at a normal rate of evaporation without preferential evaporation of either of its components, A and B, then it follows that the ratio of their evaporation rates, G_A/G_B, is proportional to their concentrations, W_A/W_B, in bulk alloy. Assuming Raoult's law for dilute solutions to be applicable, Holland /83/ applied equation (1.1) to derive the ratio of evaporation rates of components A and B in the binary alloy.

$$G_A/G_B = (W_A P_A / W_B P_B)(M_B/M_A)^{1/2} \qquad (1.4)$$

where W_A and W_B are the weight concentrations of components and P_A and P_B are their respective vapour pressures in the pure state.

As the vapourised atoms move from the source to the substrate, they may collide with each other and with the residual gas molecules of the chamber. A fraction, N_1/N_0 (say), of the initial number of vapourized atoms, N_0 will collide at distances less than a path length, d, such that

$$N_1/N_0 = 1 - \exp(-d/L) \qquad (1.5)$$

where L is the mean free path. Applying this equation W.L. Bond showed that when L is equal to the source to substrate distance d, 63 % of the atoms will collide and when L = 10d, only 9 % of the atoms will collide /84/. Therefore, the mean free path must be considerably greater than the source to substrate distance in order to ensure a straight line path for most of the emitted vapour atoms. The mean free path, L, of the air molecules can be expressed as.

$$L = (5.985 \times 10^{-3}) / p \text{ meter} \qquad (1.6)$$

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where pressure p is in Pascal. If the residual medium is air and the residual pressure, p = 6.65 x 10^{-3}Pa (= 5x10^{-5} torr) the value of L from (1.6) is equal to 90 cm. For such a value of the mean free path to ensure the rectilinear motion of vapourized atom, the source to substrate distance should be 6 to 9 cm. It is possible to put a mask between the source and the substrate to obtain a sharp pattern of the film due to rectilinear motion of vapourized atoms or molecules.

1.7 Metal-Semiconductor Junction

1.7.1 Work function of metal and semiconductor

In a metal, the electrical conduction is attributed to valence electrons. Thermal energy may allow some electrons to escape from the surface of the metal, but in general they are bound to it by the field of lattice of the atoms or positive ions. The energy with which they are held is known as the work function. This is the amount of energy required to raise an electron from the Fermi level to the state of rest outside the surface of the metal.

The work function of a semiconductor is the difference in energy between the Fermi-level and the energy of an electron at rest outside the surface. This is the energy which determines the thermoionic emission of electrons from a heated semiconductor. The electron affinity, χ_s, of a semiconductor is an important surface parameter and is the difference in energy between an electron at the bottom of the conduction band and electron at rest outside the surface /85,86/. If the bands are flat (i.e. no electric field inside the semiconductor) the work function, Φ_s, and electron affinity is related by

$$\Phi_s = \chi_s + \xi \qquad (1.7)$$

where ξ is the energy difference between the Fermi level and the bottom of the conduction band.

1.7.2 Ohmic contact to a semiconductor

An ohmic contact is defined as a metal semiconductor contact that has negligible contact resistance relative to bulk or series resistance of the semiconductor. This is the most important factor in measurement of semiconductor parameters. The important feature of such contact is that voltage drop across it must be negligible compared with the voltage

drop across the device or specimen, so that contact does not effect the I-V characteristics /87,88/.

In general, for n-type semiconductors ohmic contact can be made by using a meal with work function Φ_m less than the work function Φ_s of the semiconductor (i.e. $\Phi_s > \Phi_m$). In p-type semiconductor the work function of the metal should be greater than the semiconductor work function (i.e. $\Phi_m > \Phi_s$). However, there are few metal-semiconductor combinations which satisfy this condition.

1.8 Photoconductivity of semiconductor thin films

Photoconductivity is the process of variation of electrical resistance or conductance of a material due to illumination and the materials possessing this attributes are known as photoconductors. Generally semiconductors in bulk or thin film form, with ideal (ohmic) contacts affixed to opposite ends, are used as photoconductor. The photoelectronic properties are basically the electronic processes which are connected with photoconductivity mechanisms. The photoconduction in semiconductor is generally explained to be caused due to increase in one or combination of the parameters, viz carrier concentration, mobility and lifetime of majority carriers.

An intrinsic semiconductor with band gap larger than thermal energy, has very few charge carriers and therefore processes high dark resistivity. In dark, under the conditions of thermal equilibrium, the thermally generated carriers are distributed among the available energy states. These charge carriers occupying conduction states determine the dark conductivity of the material. This intrinsic dark conductivity σ_D is given by the relation

$$\sigma_D = q\,(n\mu_n + p\mu_p) \qquad (1.8)$$

where the different symbols have their usual signification. Due to illumination if a photon of sufficient energy acts upon an electron in the valance band and it may move to the conduction band. This process produces two carriers, an electron and a hole, both of which must ordinarily possess nonzero momentum to satisfy energy-momentum conservation in the photon absorption process. Because of this conservation maintenance, a transition occurs between the extreme edges of the conduction and valance bands, in most semiconductors, incompatible with a photon of energy equal to the band gap energy, E_g.

Accordingly it is necessary to use radiant energy, E = hv, well above E_g to produce pairs. The lowest photon energy that may create pair production is termed as the optical band gap E_B. If irradiating photons have energy substantially above, E_B then the excess energy of the carrier pairs produced is yielded to the phonons resulting in subsequent collisions. Mainly the majority carrier density is maintained by the thermal phonon carrier generation processes in the semiconductors.

When the semiconductor is illuminated by radiation of constant intensity, the concentration of mobile charge carriers due to intrinsic absorption changes to $(n + \Delta n)$ and $(p + \Delta p)$ and the conductivity under illumination is given by

$$\sigma_L = q\{(n + \Delta n)\,\mu_n^* + (p + \Delta p)\,\mu_p^*\} \qquad (1.9)$$

where μ_n^* ($= \mu_n + \Delta\mu_n$) and μ_p^* ($= \mu_p + \Delta\mu_p$) are the effective mobilities of the electrons and holes respectively.

At first usually the photo generated pairs possess energy much above the mean energy of thermal equilibrium carriers (1.5 kT). But as they interact the phonons and the crystal lattice, the photo carriers rapidly attain the temperature of the lattice; as a result the energy becomes equal to the mean thermal energy 1.5 kT. This change takes only 10^{-10}sec which is the time whose magnitude is lower by few orders to the life time of carriers. Therefore, the energy distribution of non-equilibrium carriers can be assumed to correspond to that of equilibrium carriers and hence the mobilities of these carriers don't remain the same. As a result the change in conductivity under illumination is given by

$$\Delta\sigma = \sigma_{ph} = \sigma_L - \sigma_D = q\,(\Delta n\,\mu_n^* + \Delta p\,\mu_p^*) \qquad (1.10)$$

It is obvious that Δn and Δp depend on time and level of illumination. For high dark resistivity semiconductor $p >> \Delta p$ and $n >> \Delta n$. Now photoconductivity may be due to the change in the number of carriers (Δn and Δp) or due to change in effective mobilities (μ_n^* and μ_p^*) or due to the both. The change in σ due to the change in n_e or n_h is called the 'carrier modulation' and due to the change in μ_e^* and μ_h^* is called the 'barrier modulation'. In carrier modulation, transition of carriers is caused by the photo-generated electrons in the conduction band or by photo-generated holes in the valence

band /89/. The transitions that may occur under illumination are intrinsic and extrinsic transitions. The former one is from valence band to conduction band and latter one is from donor to conduction band or acceptor to valence band. In polycrystalline thin films there exist inter grain boundary potential barriers. Due to the illumination the heights of these potential barriers are reduced and as a result the mobility of the carriers increases. In addition to the aforesaid two processes of photoconduction mechanism, a variety of photosensitive defects also contributes to the change in conductivity under the illumination.

In an extrinsic or doped semiconductor, either the acceptors or the donors mainly work for conduction and the photo conductivity is mainly either due to excitation from localized states (such as donor centers or acceptor centers) to bands (conduction or valanced) or due to excitations from trapping centers. In trapping, a carrier which is temporarily removed from a band to a localized state, eventually returned 'fast' or 'slow' to the band. The localized state is also sometimes called a sensitizing center or recombination center. The degree of localization of a state in near the band gap depends how 'deep' it lies from the band edge. The deepest states, near center of the band gap, have the most localized electronic wave functions while shallow states have wave functions extending over many lattice constants.

The trapping and recombination states occur even in intrinsic semiconductors, as a result of lattice defects. Polycrystalline semiconductors may have so many different types of lattice defect states. Dislocations are more effective as traps than that of point defects. Grain boundaries and actual crystal surface, constitute even large trapping regions. An electron trap has relativity high conduction band localized states transition probability with low localized state valance band transition probability; whereas the behaviour of a hole trap it is just opposite. Since phonon activity causes electrons to leave traps, the trapping time of a given trapping state decreases at high temperatures.

Various identifying characteristics, viz (i) dependence of photocurrent on light intensity (ii) temperature dependence of photosensitivity (iii) susceptibility to optical quenching and (iv) speed of response of a particular photoconductor depend directly on the location of energy level of the sensitizing centers /90/.

For the photoconductivity to adjust itself to abrupt changes in photo excitation intensity, needs a finite time. The shortest of this adjustment time can be the majority carrier's life time. However long adjustment times are caused by interactions, between the free and trapped charge carriers. If the density of free electrons in a photosensitive II-VI compound is larger than the density of trapped electrons near the steady state Fermi level, then the response time of photoconductor is essentially the same as the electron life time. If however the density of the free electron is much less than the density of trapped electron near the Fermi level, the measure of response time is governed by thermal release of electrons from traps. If the change of conductivity is due to ionization of donor impurities, then $\Delta n >> \Delta p$ and as a consequence the extrinsic photoconductivity is given from (1.9) as

$$\sigma_{ph}(ex) \approx q\, \Delta n\, \mu_n^* \qquad (1.11)$$

The change in carrier density, Δn can be expressed as the product of the excitation rate per unit volume, g, and carrier life time, τ, hence

$$\sigma_{ph}(ex) = q\, g\, \mu_n\, \tau \qquad (1.12)$$

Since the value of μ_n varies slightly between different materials whereas τ varies by many orders of magnitudes, it is the majority carrier life, τ that becomes the predominant photoconductivity parameter. The performance of a photoconductor is in general measured in terms of three parameters (i) the quantum efficiency or gain (ii) response time and (iii) spectral sensitivity. The long wavelength cut off in this case is given by /91/

$$\lambda_c = hc / E_g \approx 1.24 / E_g \qquad (1.13)$$

where λ_c is the wavelength in μm corresponding to the semiconductor band gap E_g in eV. In case of solid thin films the surface area is large compared with the volume of the film which results in a large surface to volume ratio. Due to strong absorption of radiation of higher coefficient near the surface or due to macroscopic deviation of periodic nature and absorbed impurity atoms, the surface recombination rate is generally high compared with that in the volume of the photoconductor.

1.9 Brief survey of previous work on CdSe thin films

The II-VI semiconductors in the from of crystal, powder and films prepared by different processes are widely investigated primarily because of their unique electronic, photo conducting and other properties, with a hope of exploring new potentialities for the fabrication of new scientific and technological devices.

At present a large number of scientists all over the world are very much concerned with the future prospect of utilizing solar energy in place of congenital fuel and electrical energy. As such thousands of researchers are studying different properties and aspects of photoconductivity material in novel ways. As CdSe, is regarded as a very prominent member of the II-IV group of semiconductor compounds, so a good number of workers are doing active research on this particular compound in both bulk and thin film form for intrinsic as well as extrinsic category under different ambient conditions. References and discussions for some of these works may be obtained from standard monographs /92-204/.

Several researchers have reported the growth pattern and characterization of Cadmium Selenide thin films under different conditions /92-103/. Hopfield /104/ investigated the excitation states and band structure in CdSe compounds. The photoconductivity of CdSe single crystal was investigated by Stupp /105/. Somorjai et al /106/ studied the interaction of Oxygen with thin films of evaporated CdSe in the temperature range 273 – 633K and developed the 'boundary layer' theory to explain the kinetic of the slow uptake of the acceptor like oxygen. It acts as an acceptor and compensates for Se vacancies resulting in decrease in dark conductivity. Sakai et al /107/ investigated photoconductive CdSe films deposited onto substrates heated from 323 to 523K and then heat treating approximately for one hour in air and in argon from 523 to 923K. He observed that unbacked films possessed low dark resistivity and poor photoconductivity, whereas backed films had good photosensitivity with increased dark conductivity. Latter on, Shallcross /108/ and Shimizus /109/ added much information to the same by studying photoconducting CdSe films. Okimura /110/ studied the photoelectronic properties of annealed CdSe evaporated films and estimated the trap density by measuring thermally stimulated current and analyzed the properties of sensitizing centers. An investigation of the electrical properties of CdSe thin film triodes

was done by Poehler and Abraham /111/ to demonstrate the existence of shallow trapping levels below the edge of the conduction band. Measurements of conductivity, Hall effect and transverse magnetoresistance were done on evaporated polycrystalline CdSe film between 80K and 700K by Janiche and Berger /112/. Study of linear and nonlinear optical properties of CdSe were conducted by Boyd et al /113/. Snejdar /114/ et al. studied the electrical conduction mechanism in thin CdSe films prepared by vacuum evaporation and annealed in Se vapour. Behaviour of Cadmium Selenide films deposited at high substrate temperature was investigated by Lubberts and Shapiro as tunneling barriers between tin electrodes /115/. Structure and photoelectric properties of thin CdSe films were studied by Svechnicov /116/ et al. Measurements of space charge limited currents had been performed on CdSe single crystals between 77K and 400K by Manfredotti et al. /117/ and they found four group of electron trapping levels with specific energies. Yodogawa et al /118/ observed that 'N-type negative differential conductivity region' arises from the temperature quenching of photoconductivity in CdSe films and suggested that there exists shallow hole trapping levels from infrared quenching effect. Effect of lithium on the formation of sensitizing processes in photoconductive CdSe films has been investigated by Ermolovich and Shtrum /119/. Several researches are there whose have studied the various physical properties of CdSe thin films regarding electrical, optical, structural etc under different ambient conditions /120-128/. An in depth study of conduction mechanisms in thin vacuum deposited cadmium selenide films were done by Chan and Hill /129,130/. They also studied the instability in conductivity of the films by extending an existing oxygen absorption model, first suggested by Somorjai. J. Hamersky /131-134/ showed the possibility of compound complex formation by the reaction of Cd and Se with oxygen particularly at high substrate temperature. He also studied the influence of the source and substrate material and of residual atmosphere during CdSe evaporation on the electrical resistance and observed that the composition of the residual gas had the most effect on the film properties. Properties of cadmium selenide films, d.c. sputtered in a mixture of hydrogen selenide and argon was studied by Glew /135/. Dhere /136/ et al studied the structure and semiconducting properties of CdSe thin films. Kutra et al /137/ studied the electrical properties of p-CdSe layers obtained by the ion implementation of Se. Naguib /138/ et al investigated the structure

and epitaxy of evaporated cadmium selenide films. Sakalas /139/ et al reported the effect of defect structure on photoconductivity of CdSe films. The phenomenon of electrical conduction and breakdown, were reported by Gogoi and Barua in CdSe films well stabilized in dry air /140/. Boichot and Wilman /141/ studied the structure and growth of thin films of CdSe condensed in vacuum on to polished stainless steel substrates initially at room temperature in residual air pressure, at normal and oblique vapour incidence. Brucker and Brillson /142/ studied reactive inter diffusion at metal-CdSe interfaces, whereas mechanism for injecting contact formation at the same interfaces were studied by Freeman and Slowik /143/. Structural, optical and photoconducting properties of sprayed CdSe films were investigated by Raturi et al /144/. Scilla and Luo /145/ studied the indium diffusion in Cadmium Selenide thin film transistors with indium gold contacts. Rosse et al studied the regeneration of CdSe thin films after oxygen chemisorption /146/. By way of photolumionsense and absorption native defects in undoped semi-insulating CdSe was studied by Rosen /147/ et al. An investigation of traps and minority carrier diffusion length in electro-deposited n-CdSe films were carried out by Pandey et al /148/ from the study of space charge limited currents (SCLC) in Au/CdSe/Ni structure. SCLC in CdSe thin films were also reported by Kalita et al /149/ for gap type configuration using Al, Ag and In electrodes. Jeffery et al /150/ studied the effect of annealing atmosphere on the properties of thin films of CdSe deposited electrochemically. Wessel and Colbow /151/ experimented on the effect of ion surface treatments on CdSe electrochemical solar cells. Roth and Burger /152/ studied the effect of Cu related defects on electron transport properties of semi-insulating CdSe. An in depth study of $CdSe_xTe_{1-x}$ thin films were done by Sebastian and Sivaramakrishan regarding the electrical conduction, oxygen absorption etc. He /153-156/ conducted an analysis on the instability in resistance and variation of activation energy with thickness and deposition temperature of $CdSe_{0.6}Te_{0.4}$ thin films deposited at high substrate temperatures. Physical properties of similar type of films was also studied by Benamar et al /157/. Gutierrez and Ortega /158/ did a comparative study of the sulphid-polysulphide and ferro-ferricyanide electrolytes in a photo-electrochemical cell with electrochemically deposited CdSe films. Raoult /159/ et al described the standardization and stabilization of resistivity-temperature characteristics of CdSe thin films by vacuum annealing. Roy

/160/ et al reported the measurements of conductivity and Hall coefficient of insulating n-type CdSe with doping concentrations near the critical concentration for the metal-insulator transition. N. Samarth /161/ et al experimented on the growth of cubic (zinc blend) CdSe by molecular beam epitaxy. Hayashi /162/ et al studied formation and the physical properties of In-doped high conductivity CdSe evaporated film. Study of photoelectronic properties of undoped /163-165/ and doped /166-169/ CdSe films were also reported by different workers. Samanta et al /170/ studied the influence of substrate temperature on the preferential orientation of CdSe film. They observed a decrease in mean disorientation angle with increase in substrate temperature both in glass and mica substrates. Levy /171/ et al studied the photoluminescence of heavily doped n-type CdSe samples with carrier concentrations above the critical concentration for the metal-insulator transition whereas Nair /172/ et al investigated the enhancement of photosensitivity in chemically deposited CdSe thin films by air annealing. Optical constants of vacuum evaporated polycrystalline Cadmium Selenide thin films over a range of 900-3100nm photon wavelengths were studied by Pal /173/ et al. and reported about the possible variation of band gap & optical constants with film thickness as well as substrate temperature. A similar type study on CdSe samples was also done by Baban et al /174,175/. Ohtsuka /176/ et al experimented on the growth of p type CdSe having zinc blend structure by molecular beam epitaxy using a nitrogen plasma source. About the two parameter scaling of hoping conductivity of n type CdSe was reported by Zhang & Sarachik /177/. Gould /178/ et al showed SCL conduction in vacuum evaporated sandwich type CdSe thin films which is dominated by exponential trap distribution, particularly at high fields and measured the trap parameters. Nesheva /179/ studied photoconductivity and recombination in single layer of Se, CdSe as well as amorphous multilayer of Se/CdSe and identified traps as well as recombination centers which controlled the transport and recombination mechanism in different temperature ranges respectively. He also reported about the preparation and characterization of amorphous SeTe/CdSe superlattices and their constituent thin layers /180/. The chemistry occurring at CdSe/Si, CdSe/SiO and CdSe/SiO_2 interfaces were investigated by Masson /181/ et al looking at very thin tapered films (0-10nm) of thermally evaporated CdSe with X-ray photoelectron spectroscopy. They also /182/ made the use of X-Ray photoelectron

spectroscopy (XPS) to characterize the thin thermal oxide film grown on single crystal CdSe (0001) and polycrystalline CdSe by exposure to oxygen (dry air) at 623K. Mohanchandra and Uchil /183/ studied the electrical properties of CdSe films deposited on vibrating substrate. Broadening of submonolayer CdSe sheets in CdSe/ZnSe super lattices was studied by X-Ray diffraction by Kyutt /184/ et al. Elango /185/ et al studied the characteristics of chemically spray deposited CdSe thin films. Thicknesses dependent properties of CdSe films deposited by hot wall technique were investigated by Veluami /186/ et al. Transition from island formation to pseudomorphic growth in the submonolayer CdSe/ZnSe multilayer system were analyzed by Kim et al /187/. Melo /188/ et al experimented on the strain relaxation during the layer by layer growth of cubic CdSe onto ZnSe. Neliaye and Youm /189/ studied the effects of post deposition processing on micro structural properties of Cadmium Selenide thin films grown from solution. Preparation and characterization of CdSe single crystal grown from the melt was done by Abd and Mongy /190/. Structure and electrical properties of high energy electron irradiated vacuum deposited polycrystalline CdSe thin films were conducted by Ion /191/ et al. Effect of thermal annealing and long term ageing on electronic defects in CdSe thin films were studied by Nesheva et. al. /192,193/ Different workers have used different methods like chemical deposition, ionic layer absorption etc for the preparation of doped as well as undoped CdSe thin films and consequently have also done the characterization and various analysis of the films from different point of views /194-204/.

1.10 Motivation of the present work

CdSe is a binary semiconductor and is considered as a prominent member of the II-VI group of semiconductor compounds on account of its potential technological importance. Because of its high photosensitive nature and suitable intrinsic band gap of 1.74eV, it is widely used in the fabrication of different optoelectronic devices like high efficiency thin film transistors, photovoltic solar cells, photodectors, light emitting diodes, filters etc. Different methods like sputtering, spray pyrolysis, solution grown and electrodeposition, vacuum evaporation etc, for preparation of CdSe films have been reported by different workers. Electrical and optical properties of semiconducting films are essential requirements for proper application in different thin film based

optoelectronic devices and these properties are very sensitive to deposition conditions as well as the techniques used. Therefore study of such properties of the thin films with respect to their different growing as well as the ambient conditions is a matter of profound importance.

Some works with regard to optoelectronic and structural properties of CdSe compound in both bulk and thin film form have been already reported. However most of the investigations were carried out using sandwich type films compared to a lesser amount of work done using gap type films. Of course, gap type film configurations are more favourable for direct photoresponse study. For the simplicity and versatility in preparing thin films, free from contamination and for readily availability of the experimental facility in our laboratory the thermal evaporation process has been used for deposition of CdSe thin films required for the proposed work where a detailed experimental investigation regarding the conductivity processes both in dark and under illumination corresponding to different structural characteristics and the level of imperfections in CdSe thin films in gap type cell configuration have been carried out. It is to be mentioned that sufficient technical data in this regard are not yet available for a comprehensive database. So motivation behind the proposed work is to supplement more relevant data on some important optoelectronic properties of PVD-TE CdSe thin films. In order to be more specific, the purpose of the present work is to make an assessment of the extent of barrier and carrier modulation processes, particularly under illumination, in thermally evaporated CdSe thin films under different ambient conditions of applied fields, illumination levels (monochromatic as well as white light) and temperatures. In course of the work from the experimental data the contribution of carrier modulation and barrier modulation to the conductivity are widely studied. The barrier modulation (i.e. the role of effective mobility particularly in photoconductivity processes) becomes a predominant factor in polycrystalline thin films. The already available data in this regard is not sufficient particularly to make point to point correlation of effective mobility with physical parameters of the polycrystalline thin films like grain boundary potential barriers, photo Pooel Frenkel conduction mechanism etc. Further attempts are also made to correlate the optical sensitivity of these thin films to other micro structural parameters like lattice constant, grain size, micro strain, dislocation density etc.

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