Abstract

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In the present work, an experimental study on structural characterization and some optoelectronic properties of thermally evaporated polycrystalline CdSe thin films under different ambient conditions was carried out. The results incorporated in the thesis are presented in five chapters as detailed below.

Chapter-I : General Introduction

Chapter-II : Equipments Used and Details of the Experimentals

Chapter-III : Structural Characterization of CdSe Thin Films

Chapter-IV : Optoelectronic Properties of CdSe Thin Films

Chapter-V : Spectral Response, Rise and Decay of Photocurrents and Optical Properties

A list of related references is included at the end of each chapter.

Chapter - I. *General Introduction*

In this chapter a comprehensive discussion is made regarding importance of CdSe thin films for the fabrication of different optoelectronic devices. Along with CdSe, relevant properties of the other II-VI group of semiconductor compounds are also discussed. A solid thin film is a homogenous material which is formed by atom by atom or molecule by molecule condensation process, whose one dimension is reduced suitably to the order of a few mean free paths of the carriers under consideration. As such thin films cannot support themselves; the condensation of a thin film is made on a suitable solid surface called the substrate. The basic physical properties of a thin film depend upon several factors.

The thickness of the films has pronounced importance as far as various physical phenomenons of the films are concerned. If the thickness is comparable to or less than the mean free path of electrical conduction process, diffusion length, effective de-Broglie wavelength etc then thickness plays a key role on different electrical as well as optical processes like electrical conductivity, optical absorption etc. In such thin films the charge

carriers invariably suffer surface collisions and thus the surface scattering process becomes a predominant factor.

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 the 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 remain in unsatisfied bond formation 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 form. In the photoconductivity processes, the imperfections play a significant role. They either act as trapping or recombination centers of carriers.

The basic quality of a thin film is dependent on its growth process. Parameters like substrate temperature, rate of deposition, source to substrate distance, vacuum level etc play significant roles in the nucleation process of the thin film growth. This influences the structural properties like crystallinity, grain size, grain boundary potential barriers etc. Optoelectronic properties of a thin film are thus strong function of structural characteristics of the film.

A great deal of research work during last few decades on binary and trinary semiconductor compounds has lead to some clarity of understanding of the physics of thin films. The existence of large number of these compounds with wide variety of different and often unique properties offers the possibility of selecting the material for different optoelectronic devices /1/. In resent years the study of optoelectronic and structural properties of II-VI group of compound semiconductors has drawn considerable interest due to their low cost of fabrication, structure sensitive properties, high absorption coefficients etc for applications in photovoltaic and photoelectrochemical devices /2/. Out of different II-VI group of semiconductor compounds CdSe is regarded as a prominent member because of its high photosensitive nature and suitable intrinsic band gap and is widely used in the fabrication of different optoelectronic devices. Different workers have studied the optoelectronic properties of CdSe thin films from different angles. The various studies on structural characteristics and optoelectronic behaviour of polycrystalline semiconductors concerning mainly the role of grain boundary potential barriers have come under increased scrutiny for a varity of potential applications /3/. Grain boundary depletion regions in polycrystalline semiconductors are relatively wide and thus these are the predominant microscale imperfections in polycrystalline thin films.

Good quality CdSe thin films can be produced by means of thermal evaporation of bulk CdSe sample onto substrates heated to elevated temperatures /4/. But CdSe thin films deposited at room temperature are mostly found to be amorphous. The thickness of polycrystalline thin films for optoelectronic devices should be greater than or equal to the effective penetration depth of the incident light and diffusion length of the photogenerated carriers. In practice this requires that the film thickness to be in the range of few tenths of a micrometer to tens of a micrometer.

All these factors have created a renewed interest for producing high quality photosensitive polycrystalline CdSe thin films. A varity of techniques have been used by different workers to produce CdSe thin films. Of these the thermal evaporation method is often preferred for its simplicity and low cost. The present work concerns with a study on the optoelectronic properties of polycrystalline CdSe thin films. The films were deposited by thermal evaporation technique under high vacuum. In this thesis the results of some experimental investigations regarding the conductivity processes both in dark and under illumination corresponding to different structural characteristics in thermally evaporated CdSe thin films is presented. It may be mentioned that sufficient technical data in this regard are not yet available for a comprehensive database. So the motivation of the present work is based on an objective to contribute more relevant technical data in regard to the important optoelectronic properties of polycrystalline PVD-TE CdSe thin films. To be more specific, the purpose of the present work is to make an assessment of the extent of carrier and barrier modulation contributions to photoconductivity under different growth and ambient conditions.

The barrier modulation (i.e. the role of effective mobility particularly in photoconductivity processes) becomes a dominant factor in polycrystalline thin films. The already available data in this regard is not yet sufficient to make some point to point correlations of effective mobility with physical parameters like grain boundary potential barriers, photo Poole-Frenkel conduction mechanism etc.

Chapter - II. ***Equipments Used and Details of the Experimentals***

In the present work thermally deposited CdSe thin films were used. Aluminium electrodes were deposited under vacuum on already deposited thin films on glass substrates to obtain gap type cell configurations. Details of the preparation technique have been discussed in this chapter. Tolansky's multiple beam interferometry method was used for the measurement of film thickness. Details of the experimental set-up have also been incorporated. An ECIL electrometer amplifier of input impedance 10^{14} ohm or higher was used to measure the voltage signals. The various experimental equipments used for electrical and optoelectronic measurements have been described. XRD and SEM analyses were used for structural and morphological studies. For elemental analysis and also to measure the stochiometry of the grown thin films WDXRF and EDAX methods were employed.

Chapter - III. ***Structural Characterization of CdSe Thin Films***

As has been already mentioned, structural characteristics of thermally deposited polycrystalline CdSe thin films influence the electrical and optical properties of the films to a great extent. Discussion on some theoretical and experimental details of XRD patterns of crystalline structure of CdSe thin films with reference to the JCPD standard have been included in this chapter. From this study it is found that CdSe thin films deposited at room temperature are amorphous and those grown at elevated substrate temperatures (T_S) are polycrystalline having hexagonal ZnS type structure. With the increase in T_S, the crystallinity of the films is found to improve. The most preferred orientation of growth of CdSe thin films is found to be along [002] direction /5/ whereas some small percentage of growth along [110] and [112] directions are also observed. Different structural parameters of the films have been evaluated and their variations as a function of T_s and film thickness have been studied.

Study of surface morphology of thermally deposited CdSe thin films carried out by using SEM analysis shows that the films deposited at higher T_S are fairly uniform, polycrystalline and free from macroscopic defects like cracks or peeling. Therefore for photoconductivity studies, the quality of high T_s grown films is quite suitable. The results of XRF spectra and EDAX analysis done on the same films show that as-deposited CdSe thin films are free from impurity, contain Cd and Se elements nearly in equal proportion. This indicates that the grown CdSe thin films are fairly stochiometric.

Chapter - IV. *Optoelectronic Properties of CdSe Thin Films*

For the purpose of optoelectronic analysis of thermally deposited CdSe thin films, initially the variation of dark current (I_D) with applied bias (V_a) has been studied to ascertain the nature of aluminium electrodes to CdSe thin films contacts. Under dark the electrode contacts were found to be ohmic for the entire range of applied bias from (-108V) to (+108V). As has been mentioned, the electrodes were formed on CdSe thin films by vacuum evaporating aluminium.

To assess the contribution of defect controlled photoconduction mechanism of the prepared CdSe thin films, logarithmic variation of photocurrent I_{ph} with intensity of illumination, Φ, was studied under both white and monochromatic illuminations. It was observed that the corresponding variation is of sublinear nature which follows the relation $I_{ph} = c\Phi^{\gamma}$, where c is a constant. The evaluated values of γ range in 0.4 to 0.7. This range of values of γ indicates that the photoconduction mechanism in these CdSe thin films is of defect controlled type.

The temperature dependence of dark (σ_D) and photo conductivities (σ_L) under different intensity of illuminations of both white as well as monochromatic lights was studied. Two distinct activation energy regions were observed in the $\ln\sigma_D$ or $\ln\sigma_L$ and 1000/T plots. The calculated values of activation energies were found to decrease with the intensity of illumination. Therefore in the observed activation regions of conductivities /6/ the mobility activation process plays a predominant role.

The dependence of photocurrent, I_{ph}, on the applied bias, V_a, shows that in the lower bias region the variation is linear whereas in the higher bias region the conductivity depends exponentially with the applied bias. Therefore this study reveals that thin films are characterized by two distinct conduction mechanisms /7/. A similar nature has also been observed in the plots of $\ln J_{ph}$ vs applied field ($F^{1/2}$) where J_{ph} is the photocurrent density. The $\ln J_{ph}$ vs $F^{1/2}$ plots are non linear in the low field region whereas in the high field regions these are linear. It is observed that with increase of light intensity the linear regions of these plots approach progressively more and more towards the low field regions. This shifting from the linear to non linear regions has been observed generally within the field regions from 85 $V^{1/2}m^{-1/2}$ to 90 $V^{1/2}m^{-1/2}$. The increase in the range of high field region linearity can be explained on the basis of reduction of average grain boundary potential barriers due to applied fields which enhances the effective mobility of the photogenerated carriers. Therefore photoconduction mechanism in these films is of the Poole-Frenkel type /8/. The calculated values of experimentally observed photo Poole-Frenkel coefficients are found to be higher than the theoretically calculated ones. This suggests the existence of some localized electric fields in the films which have values higher than the mean field.

The chapter at the end includes a brief correlative assessment of the structural analysis and photoconductivity process. As a part of which interdependence of photoconductivity on a few structural parameters has been presented for CdSe thin film samples deposited at elevated T_s.

Chapter - V. *Spectral Response, Rise and Decay of Photocurrent and Optical Properties*

Spectral response characteristics of CdSe thin films grown at different T_s were studied. The maximum photocurrent peak was observed at wavelength $\lambda = 725$ nm in all films grown at various T_s. The peak heights were found to increase with T_s and thickness of the films. An additional peak in the longer wavelength side was also observed at around 950 nm. The optical band gap corresponding to these wavelengths are 1.71 eV and 1.3 eV respectively. The observed optical absorption edge at 1.71 eV is due to direct transition of electrons from valance band to conduction band /9/. The high wavelength peak may be attributed to the native defects in the thin films.

Growth and decay of photocurrents in CdSe thin films were studied at different λ and Φ. From the photocurrent decay curves the trap depth analysis was made. The study showed that existing traps in the thin films were in the energy range 0.3 to 0.7 eV. Such traps are quite effective in changing the electrical and optical properties of CdSe thin films. These estimated trap levels are actually some defect levels. From the plots of

$\ln(I_o/I_t)$ vs time, where I_o is the photocurrent at the termination of illumination and I_t is the photocurrent at an instant of time t after termination of illumination, it was observed that there exist two different trap levels E_1 and E_2. From the evaluated values of E it was seen that there was a quasi continuous distribution of trap levels in the forbidden band. It may be noted that photocurrent in these thin films was found to obey a sublinear relation with the intensity of illumination which could be explained on the basis of defect controlled photoconductivity mechanism.

From the transmittance and absorbance spectra of CdSe thin films, deposited at different elevated T_s and of different t, the optical properties of the films were studied. The values of optical parameters were determined from the transmission spectra. The optical energy gap for the considered CdSe thin films, grown at different elevated T_s and having different t, were determined. Such type of study actually helps in characterization of optoelectronic properties of CdSe thin films.

The evaluated values of absorption coefficient α for the experimental thin films were found to be in the range 10^3 to 10^5 cm^{-1}. The calculated α were found to be quite dependent on photon energy, hν. The fundamental absorption that occurs due to allowed direct transitions is given by the relation, $\alpha = A(h\nu - E_g)^{1/2}$ where hν is the incident photon energy, E_g is the energy band gap and A is the characteristics parameter /10,11/. The present analysis of the experimental CdSe thin films showed that for all films, the dependence of α^2 as a function of the photon energy was a straight line, which indicated the direct nature of fundamental band to band transitions. The optical band gaps were found to be in the range 1.69 to 1.72 eV.