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THICKNESS DEPENDENT PROPERTIES OF n-CdSe THIN FILMS FABRICATED BY ELECTRON BEAM EVAPORATION TECHNIQUE.

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The nano crystalline semiconducting thin films of n-CdSe having different thicknesses have been fabricated on glass substrate at room temperature by electron beam evaporation technique using optimized source material. Thicknesses of the n-CdSe thin films arein the range of 600nm to 1200nm. The variations of electrical, optical and structural properties of n-CdSe thin films with thickness have been studied. The structural property of thin films has studied by X-ray diffractometer which revealsthat films have polycrystallinehexagonal structure with preferred orientation (002) plane. The surface morphology of films has also been studied by scanning electron microscope. The morphological and crystalline studies revealed that the thin film surface and crystallinity of the grains in films were improved with increase of film thickness. The optical band gaps are calculated for films using absorption coefficient. The electrical resistivity and activation energyof n-CdSe thin films are calculated by four probe resistivity measurement. Thecarrier concentration and Hall mobility of n-CdSe thin films are calculated by Hall measurement. The dependence of electrical parameters ofn-CdSe films on thickness has also been studied. Thus the thickness of n-CdSe thin film 1000 nm is optimized on the basis of structural, optical and electrical properties.

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Keywords: Fabrication & characterization, n-CdSe thin film, Thickness, Grain size, Lattice parameter

1. Introduction

The electrical, structural and optical properties of II-VI compound semiconductors have been found suitable for the preparation of semiconducting devices especially photo detector and solar energy converter. The cadmium selenide (CdSe) is one of the promising materials of this group used for fabrication of efficient multilayer thin film solar cell due to their high photosensitive property [1]. The CdSe compound semiconductor is also used in the fabrication of different optoelectronic devices [2-4]. The CdSe thin films possess n-type as well as p-type semi conductivity depending upon the type of vacancies created during deposition of thin films. The direct band gap of CdSe is 1.74 eV with hexagonal structure [5]. The quality of CdSe devices strongly depends upon electrical and structural properties of thin film fabricated with different experimental techniques. These techniques are vacuum or non-vacuum [6,7], laser ablation [8], electro chemical deposition [9], chemical deposition [10], hot wall deposition [11] and spray pyrolysis [12].The electron beam evaporation technique is suitable for the deposition of n-CdSe thin films due to high power density, wide range of controlled evaporation as well as directly evaporent material converted into vapour [13]. During the deposition process, evaporent material is placed in water cooled graphite crucible, in this process only its upper surface get high

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temperature, so metallurgical reaction between evaporent material and crucible be eliminated. This technique also provides economical and efficient use of source material.
The non-stiochiometry structure of CdSe thin film is responsible for their semi conductivity i.e. selenium vacancies or cadmium rich film exhibit n-type while cadmium vacancies or selenium rich film exhibit p-type. Keeping this in mind, the non-stiochiometry source materials were prepared with different composition of cadmium andselenium as $Cd_{1-x}Se_x$,where x varies between (0.20 - 0.50).The composition of constituent elements in source material was optimized for n-CdSe thin films on the basis of structural, optical and electrical properties [14,15].The composition $Cd_{0.60}Se_{0.40}$ was also optimized by EDAX measurement becausefilm prepared with this source material has (64.95: 35.05) average atomic percentage of cadmium and selenium. About 5% variation of composition was found in thin film with composition of optimized source material.
In present study, the n-CdSe thin film of different thicknesses have been fabricated by electron beam evaporation technique using optimized composition ($Cd_{0.60}Se_{0.40}$) of source material and studied their structural, optical & electrical properties. On the basis of these properties the thickness of n-CdSe thin film has been optimized.

2. Experimental technique

The n-CdSe thin films of different thickness were deposited at room temperature on ultrasonically cleaned glass substrate by electron beam evaporation technique using optimized composition ($Cd_{0.60}Se_{0.40}$) of source material. The pressure in vacuum coating unit (H. H. Vacuum Coating Unit-12A4) is kept below 10^{-5}torr. The films were cooled in same vacuum. Before deposition of thin film, the commercially available glass slides were boiled in chromic acid for two hours then washed using distilled water. These slides were finally cleaned with acetone in ultrasonic bath and dried at 423 K in an oven. The source material was taken in graphite crucible for deposition of film. The starting material is targeted by electron beam emitted from heated tungsten filament. Before strikes, the electron beam is deflected 180^o and accelerated at voltage 2.1kV. The evaporated particles from the crucible were deposited as thin films on the surface of glass substrate in vacuum about 10^{-5}torr. The power of electron beam gun was about 150 watts during deposition of film. During deposition of thin film, substrate was placed normal to the line of sight from the evaporation surface at different polar angle to obtain uniform deposition. The substrate was placed at distance of 12.5 cm from the crucible.About 50-100 mg of source material was used for deposition depending upon the thickness of film. In each cycle of deposition fresh material waskept in the crucible. The deposition rate and film thickness were measured using film thickness monitor (DTM-10). The sensor of DTM was attached parallel to substrate. The sensor of DTM is a quartz crystal, vibrating at frequency of 6MHz.The deposition rate 40-45 Å/ sec was kept constant during fabrication of films and controlled by current and voltage of electron beam power supply. The different thickness of the film was obtained by changing the deposition time 150-300 second. The n-CdSe thin films were characterized by measuring resistivity, activation energy and Hall coefficient.The measurement of electrical resistivity of the samples has been done using standard four probe set up and the Hall coefficient was measured by Hall set up. The both setup were designed by Scientific Equipment and Services, Roorkee, India. The galvanometric measurement has been also used to confirm the type of semi conductivity of the thin films. The EDAX measurement of thin film prepared by optimized composition ($Cd_{0.60}Se_{0.40}$) of source material has been carried out using Scanning Electron Microscope equipped with EDAX setup (Model : Carl Zeiss EVO40 Series)from advance instrument research facility, Jawaharlal Nehru University, New Delhi.The optical absorption coefficient of the n-CdSe films was recorded by placing an uncoated glass substrate in the reference beam using double beam UV-VIS spectrophotometer (Model: UV-2100) in the wave length range 400-900 nm. The spectral resolution of the spectrophotometer was 2nm throughout the experiments. The direct and indirect band gaps have been calculated using absorption coefficient. The structural property of thin films was studied with help of X-ray diffraction patterns recorded by D-8, Discover XRD-diffractometer (Bruker) using $Cu_{K\alpha 1}$ radiation (λ=1.540598Å) with Ni-filter at University of Delhi, Delhi, India. The surface morphology was studied using SEM images observed with magnification of 30,000 by

scanning electron microscope operated at 20 kV (ZEISS EVO-18, SPECIAL VERSION) at I.I.T. New Delhi, India.

3. Results and discussion

The X-ray diffraction (XRD) pattern of n-CdSe thin film of thickness 600nm to1200nm fabricated by electron beam evaporation technique on glass substrate with diffraction angle (2θ) from 20^0 to 70^0 are shown in figure 1.

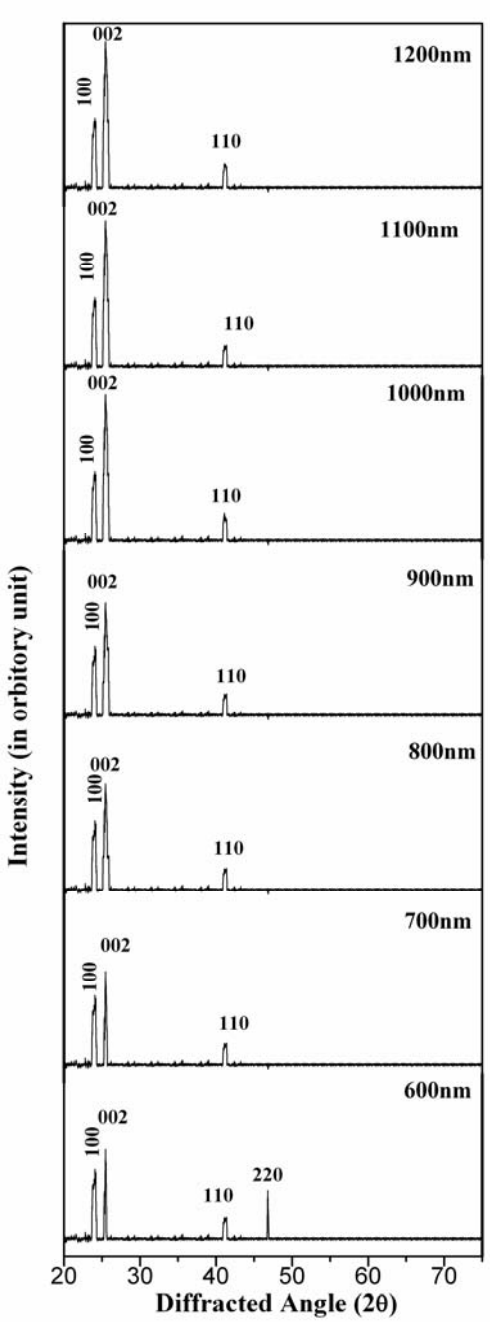

Fig. 1: XRD patterns of n-CdSe thin film of different thickness.

The (h k l) miller indices for each diffraction peak are calculated from their observed & standard d-values and compared with Joint Committee on Powder Diffraction Standard (JCPDS-*00-008-0459*) data. The XRD pattern of the films consists (100), (002),(110) and (220)

diffraction peaks which indicates polycrystalline nature. The (100), (002) and (110) diffraction peaks are corresponding to hexagonal structure while (220) is for cubic structure [16]. The (220) peak disappeared with increase of the film thickness i.e.cubic structure converted intohexagonal structure. The intensity of (002) peak increases while (100) and (110) peaks decreases with increase of film thickness. The strong diffraction (002) peak is observed foreach thickness offilm which indicates (002) plane is preferred orientation. The increase of intensity of (002) diffraction plane with the increase of film thickness maybe due to improvement of crystallinity in the films corresponding to (002) plane.

The lattice constant (c) of n-CdSe films was calculated using equation (1) [17] and given in table 1.

$$c = d\sqrt{h^2 + k^2 + l^2} \tag{1}$$

Where d is inner planar spacing and (h k l) is Miller indices.

Table 1. Thickness dependent structural parameters of n-CdSe thin films.

Thickness (nm)	Plane (h k l)	Lattice spacing 'd'(nm)	Grain size 'D'(nm)	R_C/R_B	Strain (ε)X10^{-4} (line^{-2}m^{-4})	Dislocation density (δ)X10^{14} (linem^{-2})	Lattices constant 'c'(Å)
600	002	3.89	46.46	4.15	31.70	4.63	7.77
700	002	3.87	47.05	4.20	31.30	4.51	7.74
800	002	3.88	56.17	5.01	26.20	3.16	7.76
900	002	3.86	59.59	5.32	24.70	2.81	7.72
1000	002	3.87	139.40	12.45	10.50	0.51	7.74
1100	002	3.89	139.40	12.45	10.50	0.51	7.77
1200	002	3.88	139.40	12.45	10.50	0.51	7.76

The full width half maxima (FWHM) β, dislocation density δ, strain ε and grain size D were evaluated from diffraction pattern of (002) plane for each film and also given in table-1.

The grain size of crystallite in thin film was calculated using diffractrogramme of n-CdSe thin films and Debye- Scherer's formula [17].

$$D = \frac{0.94\lambda}{\beta cos\theta} \tag{2}$$

Where λ is wavelength of X-ray (~1.540698 Å) and θ is diffraction angle.

The dislocation density (δ) in n-CdSe films was evaluated using Williamson and Smallman's formula [18].

$$\delta = \frac{n}{D^2} \tag{3}$$

Where n is a factor, which equals unity giving minimum dislocation density.

The line strain (ε) in the film was calculated by using formula[18].

$$\varepsilon = \beta cos\frac{\theta}{4} \tag{4}$$

It is also observed from XRD pattern of films that the intensity of (002) peak and its βhaveincreased slowly with increase of film thickness from 600 to 900 nm while increased sharply forfilm thickness 900nm to 1000nm and saturated for film thickness 1100 nm & 1200 nm.

It is clear from table 1 that small size of crystallite 46.46nm to 59.59nm were observed for the thin film of thicknesses 600nm to 900nm which shows that grain size increases slowly with increase of the film thickness. This small grain size was observed due to slow growth of crystallite. But large grain 139.40 nm has been observed for film of thickness 1000nm to 1200nm because of fast growth of crystallite. The large grain size, reported in present investigation, is larger than the valuesreported by other workers [11, 19, 20]. The strain in thin film is defined as the disarrangement of lattice created during their deposition and depends upon the deposition parameters. In present study, the strain decreases from 31.7 $x10^{-4}$ to $10.5x10^{-4}$ $line^{-2}$ m^{-4} with increase of n-CdSe thin film thickness. The low strain 10.50 $x10^{-4}$ $line^{-2}$ $m^{-4}$is observed for films of thickness 1000, 1100 and 1200nm which indicates better lattice arrangement in films. The dislocation is imperfection in the crystal which is created during growth of the thin film. The dislocation density decreases from 4.63 $x10^{14}$ to 0.51 $x10^{14}$ line m^{-2} with increase of film thickness. The minimum dislocation density (0.51 x 10^{14} line m^{-2}) is observed for the films of thickness1000nm-1200nm. In the present study, the observed dislocation density is lower than reported by other investigators [17, 21]. The lattice constant for n-CdSe thin film of different thicknesses 600 nm to 1200 nm is found nearly equal i.e.7.72 to 7.77 Å. The observed lattice constant in present study is in good agreement with the standard value of 7.01Å [JCPDS-*00-008-0459 data*].

SEM images, of n-type CdSe thin film of thicknesses 700 nm to 1200 nm, are shown in Fig.2. It has been found from Fig.2 that the films are fully covered, homogeneous, well adherent and free from crystal defects such as pin hole and cracks.

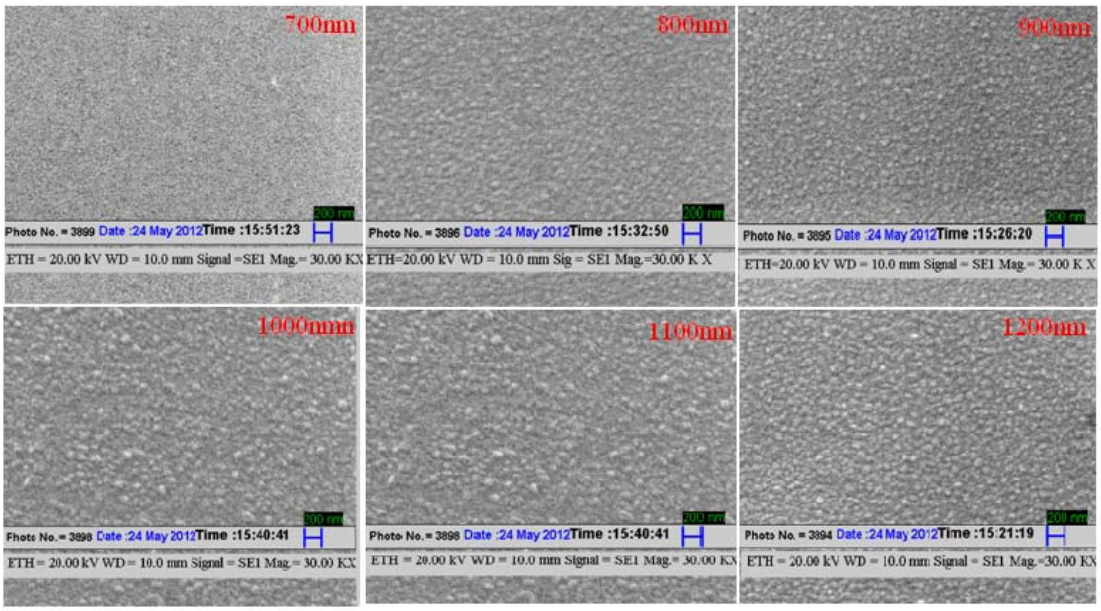

Fig. 2: SEM images of n-CdSe thin film of different thickness

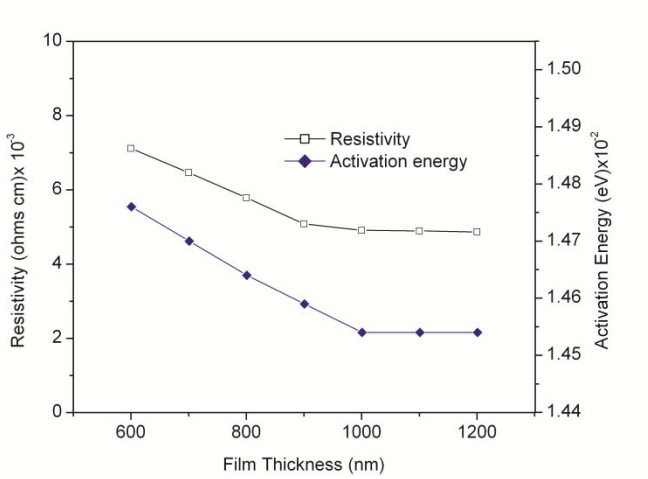

Fig. 3: Variation of resistivity and activation energy of n-type CdSe thin films with thickness.

The electrical resistivity of n-CdSe thin film of different thickness (600nm-1200nm)is measured. The Hall Effect measurement was also carried out for these films. The Hall Effect measurement shows n-type semiconducting behavior of these films. The galvanometric measurement also confirms n- type semiconducting nature of films. The variation of resistivity and activation energy with film thickness is shown in Fig.3.It is observed from Fig. 3that the resistivity decreases rapidly (7.51- 4.91) x10^{-3} ohms-cm while activation energy slowly decreases (1.480 - 1.453) x10^{-2}eV with filmthickness 600 nm - 1000 nm and saturated for other thicknesses. This decrease in resistivity of films is due to increase of carrier concentration i.e. non-stiochiometry and increase of mobility of charge carriers i.e. increase of grain size. The n-CdSe thin film exhibits n-type semi conductivity because of Se vacancies in thin film. The Se vacancies i.e. non-stiochiometry increases with increase of film thickness which is responsible for increase of carrier concentration. The decrease in activation energy with film thickness is due to shifting of donor level towards conduction band.

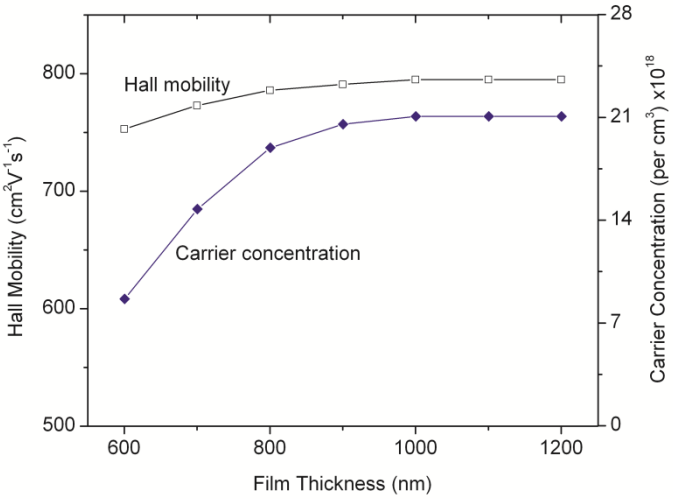

Fig. 4: Variation of Hall mobility and carrier Concentration of n-type CdSe thin films with thickness.

The variation of Hall mobility and carrier concentration is shown in Fig.4. It is observed fromFig. 4 that mobility of charge carriers increases (722 -795) cm^2/volt-sec and carrier concentration increases (1.0×10^{18} - 2.10×10^{19}) per cm^3 for films of thickness 600 nm -1000 nm.

Thereafter both became saturated for other thickness. The increase in mobility with film thickness (600-1000) nm is due to decrease in grain boundary-scattering of the charge carriers. The grain boundary scattering of charge carriers depends upon crystallite size of grain i.e. high grain boundary scattering occurs for small crystallite size while low grain boundary scattering occurs for large crystallite size.The maximum mobility of charge carriers (795cm^2/volt-sec)is observed for the n-CdSe thin film of thickness 1000 nm due to theirlarge grain size of 139.40 nm.

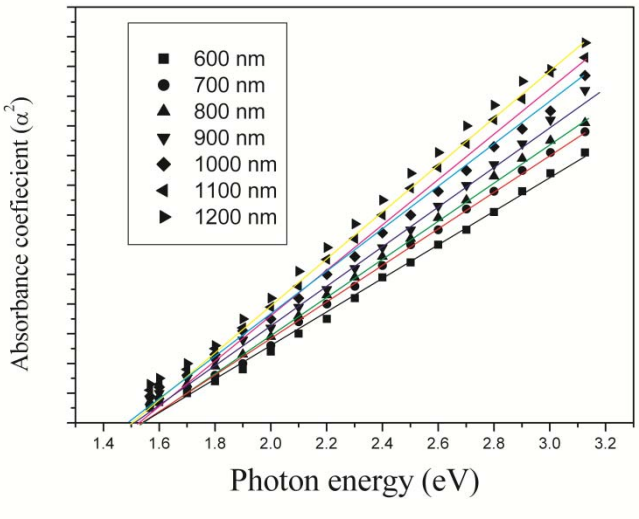

Fig. 5:Photon energy vs. square of absorption coefficient of n-CdSe thin film of different thickness.

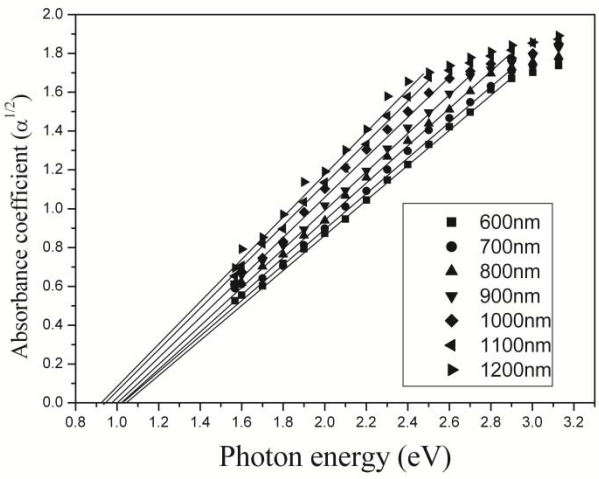

Fig. 6:Photon energy Vs Square root of absorption coefficient of n-CdSe thin film of different thickness.

The optical absorption behavior of n-CdSe thin film of different thicknesses (700nm-1200nm) is shown in Fig. 5&6. From these figures, it is observed that all these films exhibit good optical absorption in visible range (400nm-900nm). This absorption increases with increase of film thickness (700nm-1200nm) due to increase of crystallite size. The bigger size of crystallite reduces the reflectivity of incident photon on the film surface and correspondingly increases absorption due to multiple reflections. The direct energy band gap $E_g$isobtained by extrapolating the straight portion of the curve of Fig.5. The intercept portion of α_{hv}=0 line give the value of the direct band gap.The direct energy band gap of n-CdSe thin film decreases from 1.60 to 1.40 eV with increase

of film thickness.This decrease in direct band gap with increase of film thickness is due to increase in grain size of film thickness (700nm-1200nm), which can be explained on the basis of quantum size effect. It is clear from table 1 that crystallite diameter to Bohr diameter ratio (R_C/R_B) is greater than four for CdSe thin films. Hence, weak quantum size effect will be operative [22]. Similar results have also been observed for CdSe thin films by other workers [23, 24]. The indirect band gap of n-CdSe thin films is computed byextrapolating the straight portion curve of Fig.6. The indirect band gap decreases (1.01eV to 0.91 eV) with increase of film thickness.

4. Conclusion

On the basis of electrical, optical and structural parameters, we conclude that the n-CdSe thin film of thickness 1000nm has optimum parameters i.e. largest grain size 139.40 nm, high carrier concentration 2.10×10^{19} per cm^3, high mobility of charge carriers 795 cm^2/volt sec, low strain $10.50x10^{-4}lin^{-2}m^{-4}$, dislocation density $0.51x10^{14}$ line m^{-2}, low resistivity 4.91×10^{-3} ohms-cm, small direct band gap 1.48eV and small indirect band gap 0.93 eV.

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