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Surface morphological and Optical Properties of antimony doped CdSe Thin Films by Thermal Vacuum Evaporation Technique

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Abstract

Thin films having different thickness of antimony doped CdSe were deposited by thermal vacuum evaporation techniques, onto precleaned amorphous glass substrate at room temperature. The structural properties of films were evaluated by XRD, Scanning Electron Microscopy and Atomic Force Microscopy. The quantitative analysis was done by Energy Dispersive Analysis for X – Ray to determine atomic % of the material used. The X-ray diffraction (XRD) patterns of these antimony doped CdSe samples were recorded by X-ray diffractometer. The X-ray diffraction analysis confirms that films are polycrystalline in nature having orthorhombic structure with a preferential orientation along the (131) plane. The degree of such a preferred orientation was found to increase with film thickness. The lattice parameters (a = 6.469, b = 8.251 and c = 8.522) and crystallite size (D) were calculated and found to be 260.7 nm, 327.7 nm and 313.4 nm. Unit cell volume is found to be 454.87. SEM investigation confirms that films were uniformly deposited over the surface and particles were granular and circular in nature. The particle size were determined by using SEM and found to be 6.88 – 10.86 nm. The optical band gap of the films was measured by using optical absorption spectra. It is found that antimony doped CdSbSe is direct band gap material having value of 1.72 eV - 2.12 eV. The PL spectrum shows peaks in the infrared region, the bands at 825 and 970 nm are *due to a defect complex incorporating* V_{Cd}^{2-} *and* Sb_{Cd}^{+}*. Such a complex was revealed in studies of photo electric properties of CdSe (Sb).*

Keywords: *Optical band gap, thermal vacuum evaporation, XRD, SEM, AFM, EDAX.*

1. Introduction

The II–VI compound semiconductors are extremely exciting because of their uses in the optoelectronic devices and solar cells [1–7]. Among these compounds, CdSe is the most shows potential material due to its applications such as light emitting diodes, photo detectors, electrophotography, electron-beam pumped lasers, high efficiency thin film transistors and electroluminescent devices [8–10]. Key attention has been given in recent existence to study the physical properties of doped CdSe [11 - 13] thin films in order to improve the performance of the devices and also for finding new applications.

Among the many techniques engaged to prepare the pristine CdSe and Sb doped CdSe thin films, Resistive thermal evaporation method has been used due to significantly large mean free path of the vapor atoms at low pressure and a sharp thin film is obtained. This technique provides a wide window for the selection of substrate with minimum impurity concentration in the film. Toda *et. al.* [14] synthesized cadmium selenide film by thermal evaporation method. CdSe possess hexagonal (wurtzite) structure along (0 0 2) plane as confirmed from X-ray diffraction analysis. They determined lattice parameters as a = 4.30 Å and c = 7.02 Å. There was no structural transition, due to the rise in temperature during deposition process.

Most of the research that has been carried out is paying attention extensively on structural, electrical, microscopic and optical properties of binary CdSe in thin films and crystalline forms. However, very little studies presented on alloyed / doped form [15]. This paper describes the effect of antimony doping on the characteristics properties of CdSe prepared by thermal vacuum evaporation technique.

2. Experimental

2.1 Material Preparation -

The antimony doped CdSe compound ingots were obtained by taking appropriate amount of 99.999% pure Cd, Sb and Se in an evacuated quartz ampoule. The ampoule with the charge was then sealed under a pressure of 10^{-5} torr and was placed in rotating furnace. The temperature of the furnace was raised gradually to 1230 K and left at this temperature for about 12 h. Well mixed charges were then quenched in an ice bath. The CdSbSe ingot was taken out from the ampoule and made into fine powder and used for film preparation.

2.2 Synthesis and Characterization of sample

Polycrystalline antimony doped CdSe films have been deposited by thermal evaporation technique under vacuum of about 10^{-5} mbar. The substrate to source distance was kept 12 cm. The samples of different thicknesses were deposited under similar conditions. The thickness of the films was controlled by quartz crystal thickness monitor model No. DTM-101 provided by Hind-Hi Vac. Further confirmation of thickness was estimated by Tolansky's method [16] using multiple beam Fizeau fringes. The deposition rate was maintained 10 - 20 Ǻ/sec throughout sample preparation. Before evaporation, the glass substrates were cleaned thoroughly using concentrated chromic acid, detergent, isopropyl alcohol and distilled water.

X – Ray diffractogram (Bruker, Germany) were obtained of these samples to find out structural information and to identify the film structure qualitatively. The scanning angle (2θ) range was from 20^0 - 80^0 (CuK$_\alpha$ line). Surface morphological studies of the thermally deposited antimony doped CdSe thin films were done using the Scanning Electron Microscope (Zeiss) operating with an accelerating voltage 15 kV and Atomic Force Microscopy (AFM). The quantitative compositional analysis of the CdSe films were carried out by EDAX (Energy dispersive X-ray Analyzer) technique attached with the SEM. Optical absorption was measured by UV-VIS spectrophotometer model no. Shimadzu - 2450.

3. Results and Discussions:

3.1 Structural characterization-

Fig. 1 (a - c) shows the XRD pattern of antimony doped CdSe thin film prepared at substrate temperature of 303K. The X-ray diffraction (XRD) analysis revealed that the films are polycrystalline in nature possessing orthorhombic structure. It can be seen that the film thickness strongly affects the XRD pattern. For lower thickness, the films have random particle orientation, identified by the presence of various peaks at (102), (101), (131), (023) and (040). As the film thickness increases, the (1 3 1) diffraction peak becomes more and more dominant. This means that, during the atomistic condensation of the film formation, the deposited atoms are at random orientation. As the thickness of the film increases the polycrystalline grains begin to orient mainly along (1 3 1) direction which is evident from the Figs. 1(b & c). The crystallite size was evaluated using well known Scherrer's formula and found to be 260.7 nm, 313.4 and 327.7 nm for the thickness 1000 Å, 2000 Å and 3000 Å resp. The unit cell volume was found to be 454.

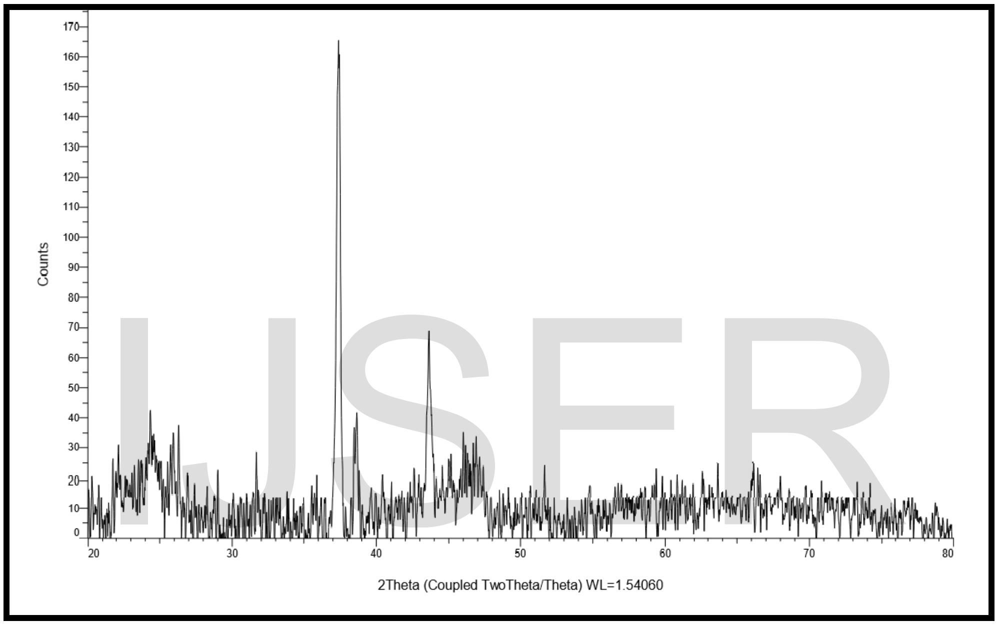

Fig. 1(a) XRD of CdSbSe of thickness 1000 Ǻ

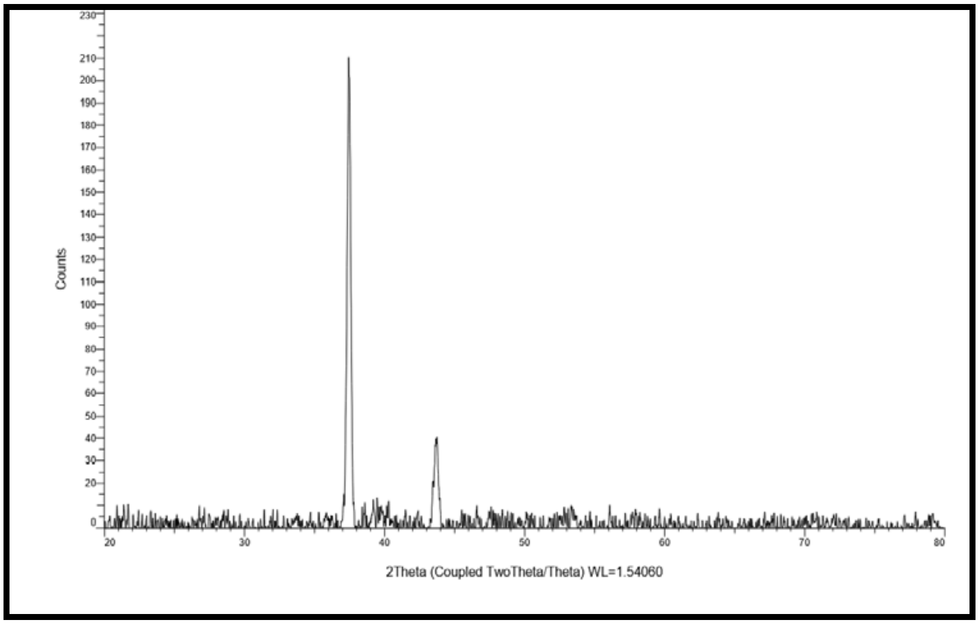

Fig. 1(b) XRD of CdSbSe of thickness 2000 Å

Fig. 1(c) XRD of CdSbSe of thickness 3000 Å

3.2 Morphology Observations

The SEM image of CdSbSe thin film show that the film is uniform, polycrystalline, well cover on glass slide and free from microscopy defect like cracks or peeling. Nano size grains were uniformly distributed over smooth homogeneous background. The particle size were found to be 6.88 - 10.86 nm

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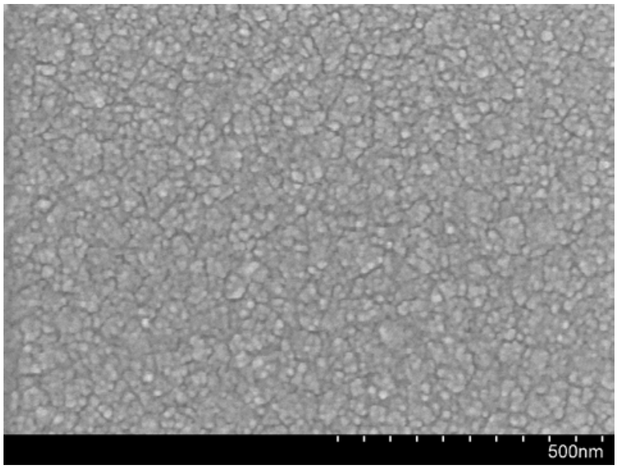


Fig: 2(a) SEM image of CdSbSe thin film (2000 Å)

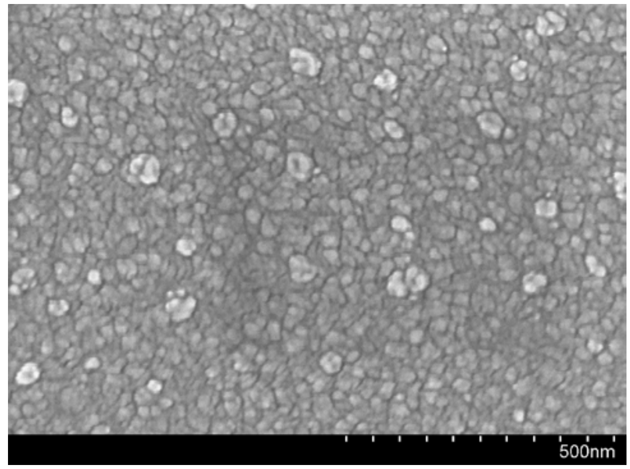
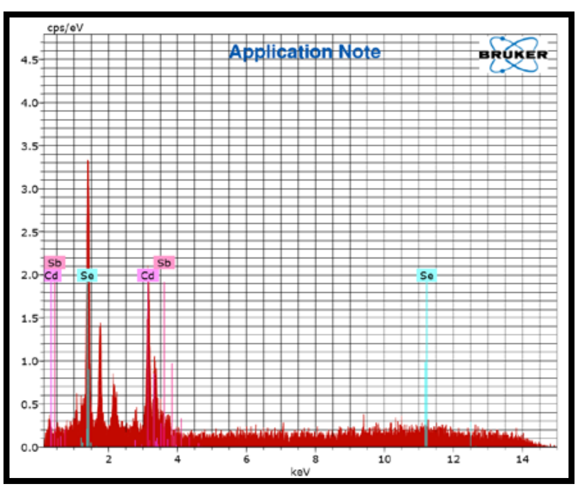


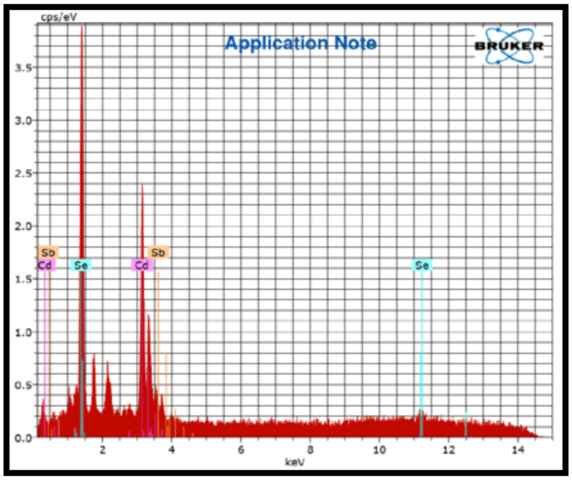
Fig: 2(b) SEM image of CdSbSe thin film (3000 Å)

3.3 Elemental Analysis

The EDAX spectral analysis for the antimony doped CdSe thin film prepared by thermal evaporation technique is shown in Fig.3.The obtained percentages of the constituent elements in all investigated films indicate that samples are nearly nonstoichiometric. The obtained result gives support for the quality of the prepared antimony doped CdSe films by thermal evaporation technique. It is found that the prepared films are selenium rich due to difference in vapors pressure of CdSe and Sb.



(a)



(b)

Figure: 3 (a, b) EDX spectrum of nanocrystalline CdSbSe

Figure (4, 5) represent the two-dimensional (2D) and three dimensional (3D) topographic images of antimony doped CdSe films prepared by thermal evaporation technique onto glass substrates. The film matrix was found to have some granular / circular particles embedded into the background fine grained matrix. These granual particles may be due to the CdSe: Sb agglomerates deposited over the uniformly spread CdSe nano particles. Our investigations showed that the grain size determined by means of AFM ranged between 10 - 30 nm in the matrix. The roughness of the film surface is small. This will provide valuable information on the height deviation of the roughness profile and on its lateral distribution. From the line profile analysis, the average roughness values calculated and found to be 3.6 nm for the CdSbSe films deposited at RT. These observations show that CdSbSe films deposited at RT have the device quality surface which will be suitable for developing PEC solar cell devices.

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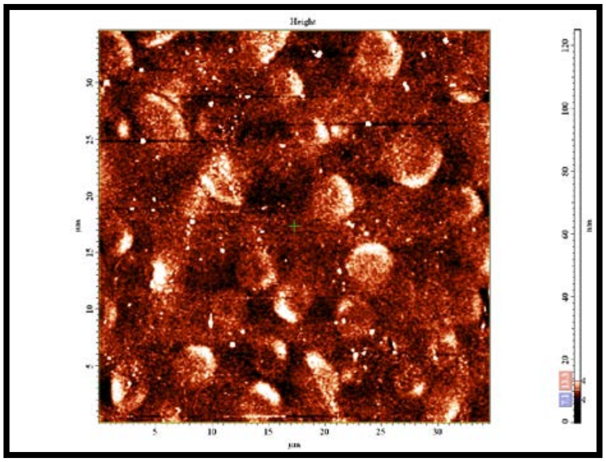


Fig. 4 2D AFM image of CdSe: Sb film

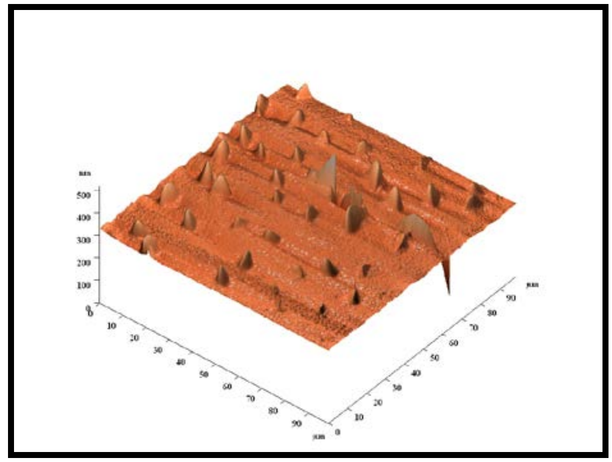


Fig. 5 3D AFM image of CdSe: Sb film

3.4 Optical properties of CdSe thin films

The spectra displayed in Fig. 6 transmittance spectra. The film transmits well in the visible region of the solar spectrum. The optical band gap of these films has been calculated using the relation (Tauc 1974).

$$\alpha h\nu = A\,(h\nu - E_g)^n$$

where, hν is the photon energy, a the absorption coefficient, Eg the band gap, A is constant and, n = 0· 5 for direct band gap material, n = 2 for indirect band gap material. The plot of $(\alpha h\nu)^2$ versus hν for these CdSe:Sb films is presented in Fig. 7 This figure clearly shows the linear dependence for the value of P =1/2. This is attributed to an allowed and direct transition with direct band gap energies. The observed trend at absorption edge towards lower photon energies for the increasing film thickness could be attributed to the change in the grain size and the stoichiometric. The straight line portion is extrapolated to cut the x-axis, which gives the energy gap. All graphs show straight line portions supporting the interpretation of direct band gap for all the films. The red shift of the absorption edge in Sb doped CdSe has been attributed to the charge-transfer transition between the antimony ion 5p-electrons and the CdSe conduction or valence band. Sb dopant may form a dopant energy level within the band gap of CdSe. The electronic transitions from the valence band to the dopant level or from the dopant level to the conduction band can effectively red shift the band edge adsorption threshold [17].The CdSbSe layer has the transmittance between 65% - 95% at wavelengths longer than the absorption edge. The evaluated band gap energies are given in Table - 1 which clearly indicates the dependence of band gap on thickness of the films. The estimated band gap values were in good agreement with those published in the literature for CdSbSe. It is observed that the band gap decreases with increase of film thickness. Hence the CdSbSe can be used in development of efficient photovoltaic application.

Table -1 Variation in band gap with thickness

Thickness (Å)	Band gap energy (Eg) eV
1000	2.12
1500	1.86
2000	1.84
2500	1.78
3000	1.72

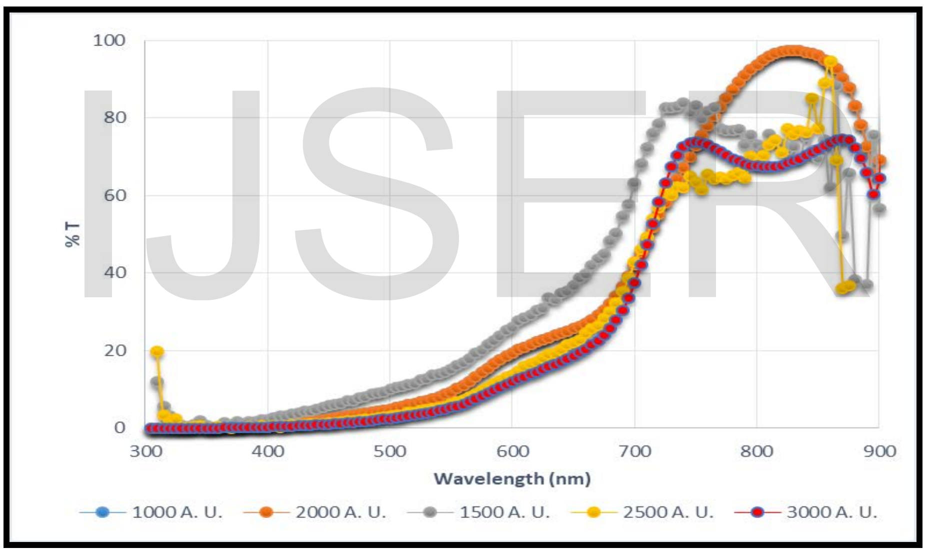


Fig. 6. Plot of transmittance vs. wavelength.

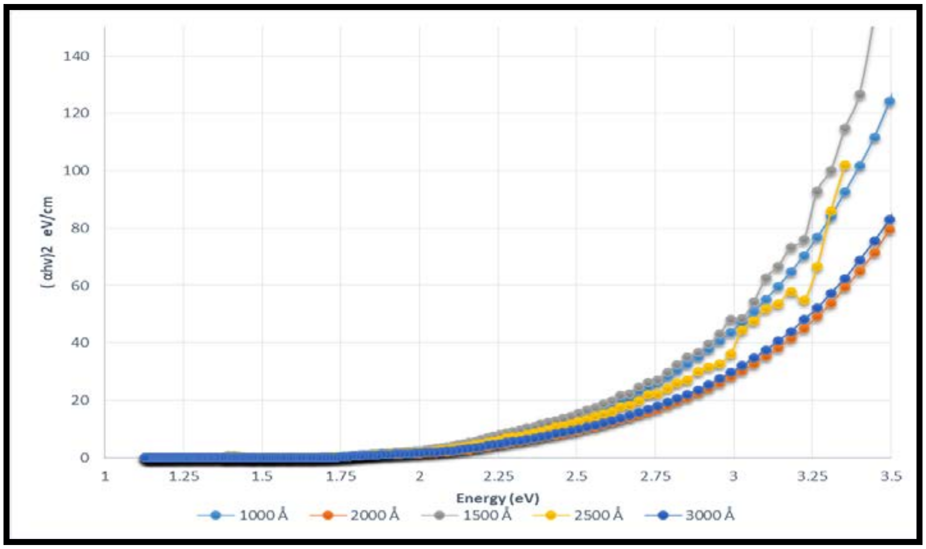
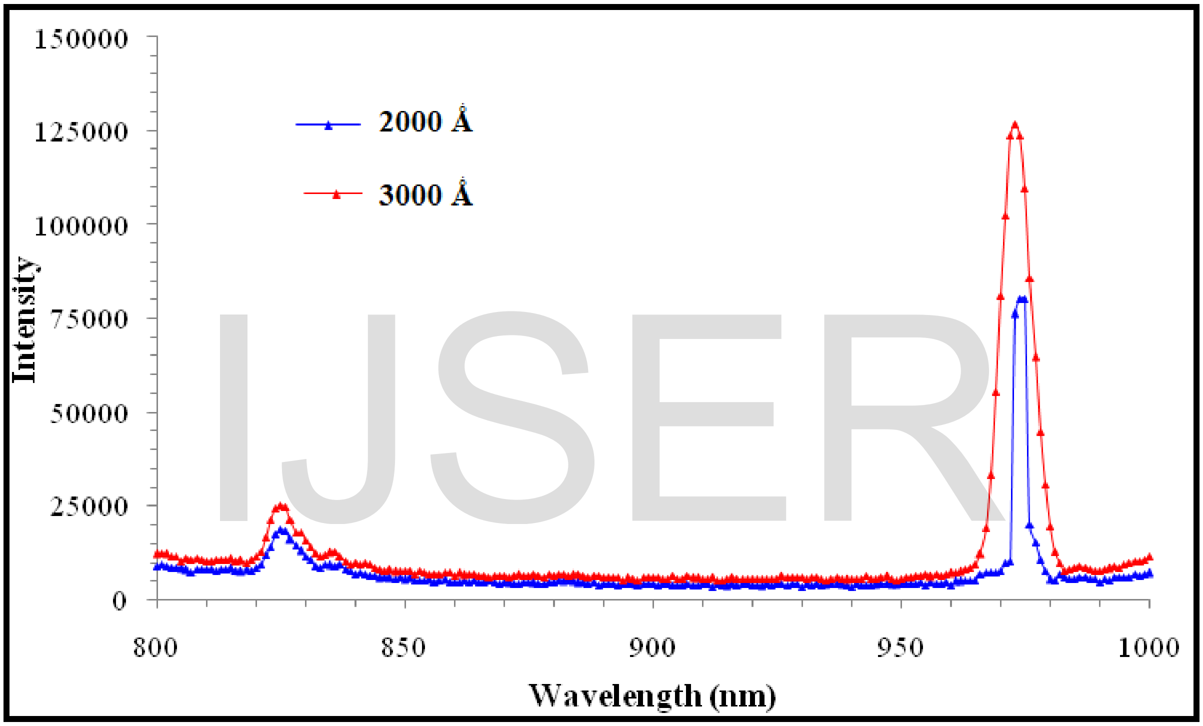


Fig. 7. Plot of $(\alpha h\nu)^2$ vs. hν

3.5 Photoluminescence Properties

To reveal emissions related to the dopants, we compared the luminescence spectra of antimony doped CdSe. The introduction of dopant (Sb) into CdSe causes transformation in the PL spectrum, due to generation of shallow levels in the band gap. The PL spectrum shows peaks in the infrared region, at 825 and 970 nm. The intensity of these lines increases sharply with increasing thickness. We assume that the bands at 825 and 970nm are due to a defect complex incorporating V_{Cd}^{2-} and Sb_{Cd}^{+}. Such a complex was revealed in studies of photo electric properties of CdSe (Sb).



4. Conclusions

Antimony doped CdSe thin films of different thickness have been deposited successfully on glass substrate with different thicknesses. XRD confirms that the structure of the film is polycrystalline in nature and having orthorhombic structure. From SEM study it is observed that deposited CdSbSe film were homogenous and granular/circular structure with nanocrystalline in nature. The particle sizes varying from 6.88 to 10.86 nm. From AFM study it is observed that surface image is homogeneous and well-connected grains. Analysis of the transmission data for CdSbSe thin films, deposited at RT, showed the energy band gap, Eg, in the range of, 1.72 eV - 2.12 eV, hence the CdSbSe can be used in development of efficient photovoltaic application in the next phase of work. The PL spectrum shows peaks in the infrared region, the bands at 825 and 970 nm are due to a defect complex incorporating V_{Cd}^{2-} and Sb_{Cd}^{+}. Such a complex was revealed in studies of photo electric properties of CdSe (Sb).

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