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Hydrophobic Cdse: Sb Thin Films by Chemical Spray Pyrolysis Technique

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Abstract: ***In the present paper, influence of antimony (Sb) in CdSe thin films has been investigated. Pristine and Sb doped CdSe thin films have been deposited using homemade chemical spray pyrolysis unit. Both films have been found to be polycrystalline in nature and possess cubic sphalerite structure. Sb doped CdSe films have extended a red shift (52 nm red shift for 10 wt% Sb) compared to pristine CdSe film. The decrease of average crystallite size and increase of average surface roughness has been observed with Sb doping into the host CdSe thin films. The water contact angle has found to increase from 77.33° to 123.74°, which indicates that the surface wettability of the CdSe thin film is changed from hydrophilic to hydrophobic nature by the antimony.***

Keywords: Semiconductors, Spray Pyrolysis, Crystal structure, Optical properties and Surface properties.

1. Introduction

Cadmium selenide (CdSe) is an important member of II-VI group of binary compounds which have many applications like high-efficiency thin film transistors [1,2],solar cells [3,4],photoconductors [5]and gas sensors[6,7]. Key attention has been given in recent years to study the physical properties of doped CdSe [8, 9 & 10] thin films in order to improve the performance of the devices and also for finding new applications.Among the many techniques employed to prepare the pristine CdSe and Sb doped CdSe thin films, Chemical Spray Pyrolysis is an attractive method for deposition of large-area films due to its simplicity and low cost. For the first time, we would like to emphasize on the modification induced by the variation of antimony doping rate on the structural, optical, and surface properties of sprayed CdSe films.

2. Experimental

Pristine and Sb doped CdSe thin films were deposited on glass substrate by the chemical spray pyrolysis method using aqueous solution prepared from 0.1 Mof cadmium acetate and selenium dioxide. Compressed air was used as a carrier gas. Double distilled water was used as a solvent.The resulting solution was doped with antimony tri chloride. Before deposition, glass substrate was ultrasonically cleaned in acetone, ethanol and double distilled water, successively. In each deposition, the nozzle to substrate distance was maintained at 28 cm and 80 mL of precursor solution was sprayed at a rate of 3 mL/min on ultrasonically cleaned glass substrate maintained at an optimized temperature of 250°C.

X-ray Diffraction (XRD) pattern of the deposited thin films was recorded in order to identify the phase purity and structure using Bruker powder X-ray diffractometer with Cu K_α radiation. Energy Dispersive X-ray analysis (EDAX) was carried out using analytical system attached with SEM, which is the direct evidence of the presence of Sb in the host CdSe thin films. The 2D and 3D topography of the prepared films were elucidated by atomic force microscopy (AFM) (Non contact mode, A100 SGS, APE Research).The optical absorption spectra were studied with UV-Visible spectrophotometer (SHIMADZU UV-1800). Wettablity test was performed by contact angle analyzer (Holmarc).

3. Results and Discussions

The structure, phase purity and crystallite size of the thin films were determined from the XRD pattern, as shown in Fig.1.In all the cases, observed diffraction peaks were indexed to cubic sphalerite phase structure (JCPDS no.19-0191).

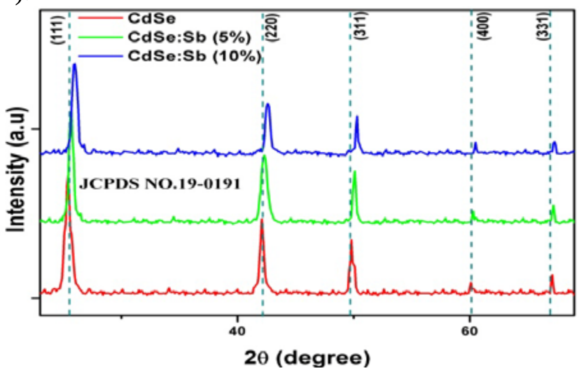

Figure 1: XRD pattern for pristineand Sb doped CdSe thin films

In pristine CdSe, the Bragg peaks were observed at 25.371, 42.040, 49.731, 60.981 and 67.132 due to (111), (220), (311), (400) and (331) planes of cubic sphalerite phase. For the doped CdSe thin films, XRD pattern indicates no visible secondary phases or impurity peaks which demonstrates that the dopant is well integrated into the lattice sites during the synthesis process. In order to see the impact of the dopant ions in the CdSe lattice, peaks of cubic sphalerite were analyzed. Peaks are shifted to higher angles with increasing Sb concentration compared to those of pristine CdSe (Fig. 1).

Table 1: The average crystallite size,band gap,contact angleof pristine and Sb doped CdSe thin films.

Sample Name	Avg. Crystallite size (nm)	Band gap (eV)	Contact angle (deg.)
Pristine CdSe	32.20	1.95	77.33
CdSe: Sb (5 wt%)	28.40	1.87	94.21
CdSe: Sb (10 wt%)	23.20	1.78	123.74

The minor peak shift is usually assigned to the successful incorporation of dopant ions in the host matrix.The lattice constant of 10 wt% Sb doped CdSe (a = 6.000 Å) is found to be slightly smaller than those of pure CdSe (a = 6.077 Å). The smaller ionic radii of Sb ions (0.90 Å) compared to Cdions (1.09 Å) in the cubic coordination, tends to decrease the size of the lattice in doped CdSe thin films. The size of the crystallite was evaluated from the high intense peak of the X-ray diffraction pattern using the Debye-Scherrer formula. The decrease of average crystallite size has been observed with Sb doping into the host CdSe thin films (Table.1).The decrease of crystallite size with increase of Sb concentration is due to the replacement of Cd ions by low ionic radii of Sb ions in the CdSe crystal lattice [11].Similar tendency in the crystallite size reduction of ZnO with the increase of Al concentrations, due to the replacement of Znby Alions in ZnO crystal lattice was reported by Suwanboon et al. [12].

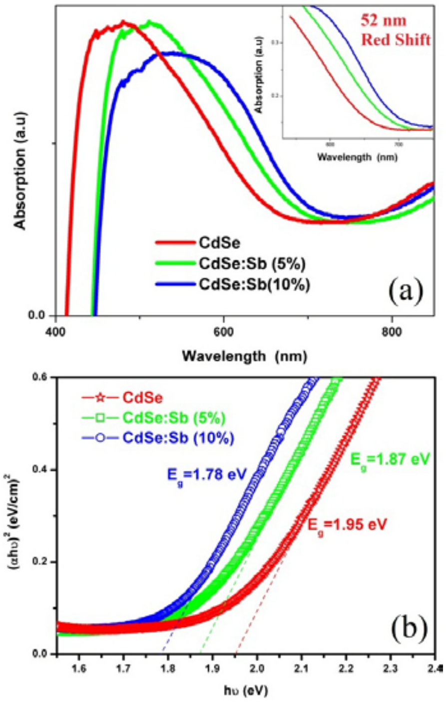

Figure 2: (a).Absorption spectra, (b) Band gap plot of pristineand Sb doped CdSe thin films.

The absorption spectra of pristine and CdSe: Sb thin films as a function of Sb wt% were studied in the wavelength range 200 to 900 nm (Fig. 2 (a)). It is apparent that the absorption spectra of all the Sb doped CdSe have extended a red shift compared to those of pristine CdSe. Particularly the 10 wt% Sb doped CdSe film has extended a 52 nm red shift which is shown in inset Fig. 2(a). 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. The optical band gap (Eg) of the prepared thin films have been obtained from the Tauc plot (Fig. 2(b)) and it comes out to be 1.95, 1.87 and 1.78 eV (Table.1) for pristine, 5 wt% and 10 wt% CdSe thin films respectively. The decrease of Eg has been observed with Sb doping into the host CdSe thin films.

The peaks of Cd, Se and Sb have been observed, which confirm the presence of Sb in the host CdSe thin film. Also, no traces of any other impurity elements have been observed in the samples. EDAX measurement reveals 5.04% and 10.23% Sb for 5 wt% and 10 wt% doping concentration, consistent with the weight percent of Sb added.

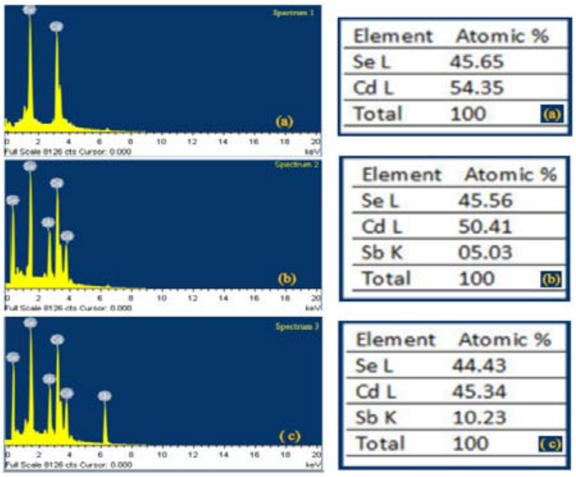

Figure 3: EDAX. (a) Pristine CdSe, (b) 5 wt% Sb doped CdSe and (c) 10 wt% Sb doped CdSe

From Fig. 3, it is observed that there is a decrease in the Cd concentration due to the replacement of Cd by Sb in CdSe film. So antimony incorporation may occur by occupying the cadmium site in the host CdSe thin film.

Fig. 4 (a, b, c) represent the two and three-dimensional topographic AFM images of pristine and Sb doped CdSe thin films. For a detailed study on average roughness of CdSe surface and their variation with Sb concentration, line profiles were recorded. From the line profile analysis, the obtained average roughness values are 1.86, 2.20 and 6.10 nm for pristine and (5 & 10 wt%) for Sb doped CdSe thin films respectively. Minimum average surface roughness value (1.86 nm) is observed for pristine CdSe thin film (Fig. 4 (a)). It is found that the incorporation of antimony results in an increase of surface roughness of the CdSe thin films from 1.86 to 6.10 nm.

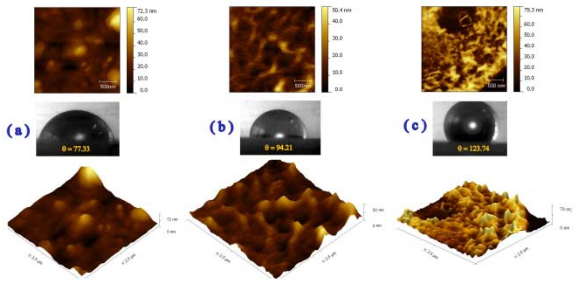

Figure 4: AFM &Contact angle measurement. (a) Pristine CdSe, (b) 5 wt% Sb doped CdSe and (c) 10 wt% Sb doped CdSe

In order to investigate the surface properties of the CdSe thin film following the addition of Sb, the wettability of the CdSe thin film was characterized by contact angle measurements. Wettability test gives information about the interaction between a liquid and a solid in contact angle. The hydrophobic or hydrophilic nature of the materials is confirmed by the wettability test. Higher wettability results in a smaller contact angle with the surface and indicates a hydrophilic nature and vice versathe contact angle (θ) between a flat solid surface and a liquid droplet is given by Young's equation[13].

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \text{ - - - - - - } 1$$

Where γ_{SL}, γ_{SV}, and γ_{LV}denote the interfacial tensions of the solid-liquid, the solid-gas, and the liquid-gas interfaces, respectively. Contact angle measurements were carried out for all the prepared samples and are summarized in Table 1. The contact angle is found to increase from 77.33° to 123.74°, as shown in Fig. 4, which indicates that the surface wettability of the CdSe thin film is changed from a hydrophilic to hydrophobic nature by the addition of antimony. Moreover, surface roughness of the sample plays an equally important role in the wettability of a surface. Shibuichi et al. showed that the contact angle can also be tuned by the solid roughness in the hydrophilic region [14]. It is found that the addition of antimony results in an increase in contact angle of the CdSe thin films from 77.33° to 123.74°, which can be explained by the high surface roughness induced by antimony [14].Hence, the surface roughness of the film may proportional to the contact angle of the CdSe: Sb film.

4. Conclusions

The pristineand Sb doped CdSe thin films have been deposited successfully using homemade chemical spray pyrolysis unit. In all the cases, observed diffraction peaks were indexed to cubic sphalerite structure. The lattice constant of Sb (10 wt%) doped CdSe (a = 6.000 Å) is found to be slightly smaller than those of pure CdSe (a = 6.077 Å). There is a decrease in the average crystallite size with increase of Sb content in CdSe thin film. From optical absorption spectra, all the Sb doped CdSe films have extended a red shift compared to those of pristineCdSe film. Particularly the 10 wt% Sb doped CdSe film has extended a 52 nm red shift. AFM measurements reveal that the average surface roughness of the film increases from 1.86 nm to 6.10 nm.Moreover CdSe thin film is changed from hydrophilic to hydrophobic nature after the incorporation of Sb.

5. Acknowledgements

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