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RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION OF CdSe THIN FILMS DEPOSITED AT ELEVATED TEMPERATURES BY CHEMICAL BATH DEPOSITION

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ABSTRACT

Cadmium selenide (CdSe) thin films were deposited on glass substrates by the chemical bath deposition (CBD) method, using cadmium sulphate ($CdSO_4$) and sodium selenosulphite (Na_2SeSO_3) as sources of cadmium and selenium ions respectively. The influence of bath temperature (T_b), on the structural, morphological, chemical composition and optical properties of these films were investigated. XRD studies revealed that the film deposited at 323K was polycrystalline with hexagonal structure and exhibited (100) preferential orientation. The film deposited under optimum conditions (T_b = 50°C, t_d = 2 hr and [Cd]/[Se] ratio = 3:1) was relatively well crystallized. Their surface morphologies were composed of small grains with an approximate size of 13 nm and grains grouped together to form large clusters. EDAX analysis revealed that these films were nonstoichiometric with a slight selenium deficiency. The optical band gap was found to be 1.72 eV.

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INTRODUCTION

Thin films of group (II-VI) compounds have been widely investigated primarily because of their size-dependent structural, morphological, optical, and electronic properties arising from the quantum confinement of electrons and large surface-to-volume ratio of nanoparticles (Zhang and Li, 2004; Zhu *et al*., 2000; Coe *et al*., 2002; Gorer and Hodes, 1994; Empedocles , 1999; Ludolph *et al*., 1998). Among these, CdSe (E_g, bulk 1.74eV), group (II-VI) nano particles have received considerable attention because of their tunable band gap, which can vary their optical response from the infrared region to the ultraviolet, and their major contribution to solar cells, photo electronics, light amplifiers, thin film transistors and single-electron transistors, light emitting diodes, and lasers. (Sharma *et al*., 1992) Among the various applications, cadmium selenide has been studied intensively in recent years as a photo anode in photo electrochemical (PEC) cells. (Gutierrez and Ortega, 1989) The conversion efficiency of these cells as well as the physicochemical stability of the anode in an electrolyte system depends critically on the structure and composition of the CdSe films. An essential criterion for obtaining high efficiency from PEC cells is the use of the CdSe photo anode as a thin film with large crystallites in preferably a hexagonal crystalline phase. The larger crystallites inhibit photo carrier losses due to grain boundary recombination, and the hexagonal phase has a higher photo absorbance and provides much needed stability against corrosive electrolyte in PEC cells. (Bouroushian *et al*., 1993) Among various other methods, the chemical bath deposition (CBD) method is found to be an inexpensive, simple, and convenient method for depositing large area nanocrystalline thin films at relatively low temperatures. A number of researchers have deposited CdSe thin films using the CBD method and reported different types of crystal structures, i.e., amorphous, (Shaw and Parkin, 2001; Garcia *et al*., 1996; Cachet *et al*., 1995) cubic (Zhu *et al*., 2000; Yochelis and Hodes, 2004) a mixture of cubic and hexagonal (Rincon *et al*., 2001; Palchik *et al*., 2001) and hexagonal. (Crouch *et al*., 2003; Nair *et al*., 2004) Thus structural phases and properties of CdSe films prepared by the CBD method were critically dependent on various preparative parameters such as the sources and concentration of metal and chalcogenide ions, pH of the resultant solution, deposition time, temperature, and thickness.

MATERIALS AND METHODS

Cadmium sulphate was purchased from LOBA Chemicals. 30% ammonia solution and triethanolamine were procured from Merck. All chemicals were used as purchased. Sodium selenosulphate (Na_2SeSO_3) was prepared by heating selenium

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powder with a solution of sodium sulphite (Na_2SO_3) in water at 90 °C with constant stirring.

Deposition of CdSe thin film

A 10 mL of 0.3 M cadmium sulphate ($CdSO_4$) solution was mixed with 30% ammonia solution. A white turbidity appears which was dissolved in excess of ammonia solution. After dissolving the turbidity 10 mL of 0.1 M sodium selenosulphate was mixed with the solution. With this 12 mL triethanolamine was mixed with constant stirring. Then the solution was transferred to a 100 mL beaker in which glass plate were suspended horizontally. Three systems were made and were kept at 313K, 323K and 333K bath temperature for two hours without disturbing. The CdSe thin film deposited on clean glass plate were rinsed in double distilled water, and dried in air.

Characterization

UV-Vis spectra or reflectance were recorded by using a U-4100 spectrophotomter (Hitachi). X-ray diffraction (XRD) patterns were recorded on SIEMENS D5005 X-ray diffractometer with CuKα radiation. The Atomic percentage compositions and Surface morphology analysis were carried out by using high resolution Zeiss (Sigma-VP) scanning electron microscope (SEM) attached with Energy dispersive X-ray analyzer (EDX) at IASST. The operating accelerating voltage was 5 kV at different magnifications and working distance was 6.9 mm for as-prepared thin films and 5.4 mm for films prepared at elevated temperature. The thickness of the film was measured by weight difference method assuming the density of the deposited film to be same as that of the bulk. The film thickness varied with deposition time.

RESULTS AND DISCUSSION

The thickness of the film in a single dipping was estimated by gravimetric method. According to gravimetric method the film thickness can be calculated as; Thickness (t) = M/Ad Where M= Mass of the thin film, d= Density of CdSe and A= Area of film. The value of density of CdSe = 5.816 g/cc. Thus knowing the value of M, d and A of the thin films, the thickness were calculated.

Structural Characterization

The XRD pattern of the CdSe thin films prepared at different bath temperature were shown in Figure 1 to Figure 3. From X-ray diffraction spectra, no well defined peaks were observed for the film (PSA) prepared at 313K (Fig. 1) and hence the peaks were not indicated in the spectra. This showed that the film was amorphous in nature. Again for film (PSC) prepared at 333K though peaks appeared but they were not so prominent (Fig. 2). The peak positions when compared with JCPDS Data Card No: 08-0459 indicated hexagonal phase (wurtztite) of CdSe thin films. Also the intensity of the peaks indicated poor crystalline nature. This may be due to the rapid precipitation of bath components at higher temperature which was observed during preparation. Only well defined peaks were observed for the CdSe thin film (PSB) prepared at 323K (Fig. 3). When compared with JCPDS Data Card No: 08-0459, indicated hexagonal structure of CdSe thin film at 323K with preferred orientation in (100) plane. This kind of phase transformation of CdSe thin films at higher temperature as compared to room temperature (cubic phase) can be attributed to various reasons like, increase in crystallinity, decrease of pH with the evaporation of NH_3, change in atomic configuration etc. Since well defined peaks were observed only for CdSe thin films synthesized at 323K, hence further characterization was carried out only for PSB film. The various structural parameters determined for CdSe thin film (PSB) was given in Table 1. The crystallite size, dislocation density and d values for different planes were calculated in the same way as in the previous case.

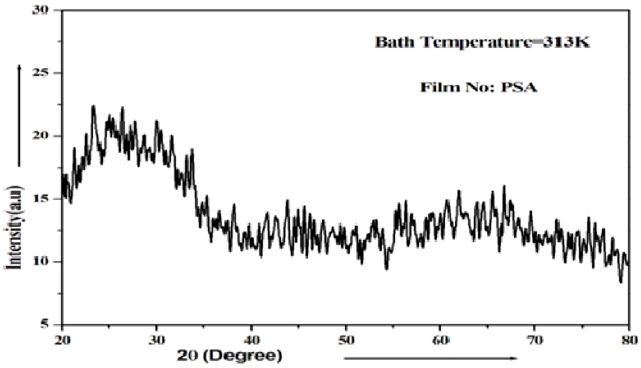

Figure 1. X-ray diffraction pattern of a CdSe film at a bath temperature 313K showing the amorphous nature of the film (Film No. PSA)

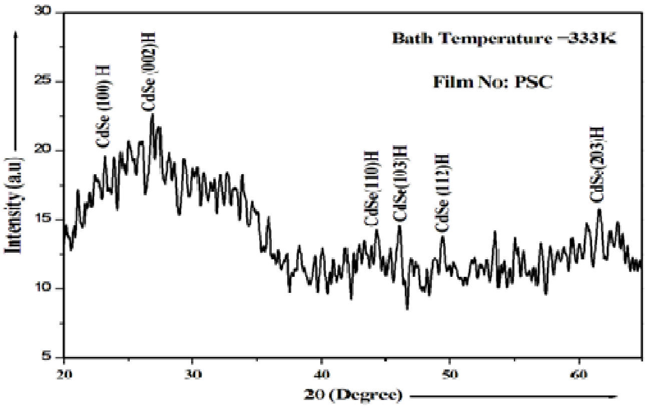

Figure 2. X-ray diffraction pattern of a CdSe film at a bath temperature 333K showing the amorphous hexagonal nature (Film No. PSC)

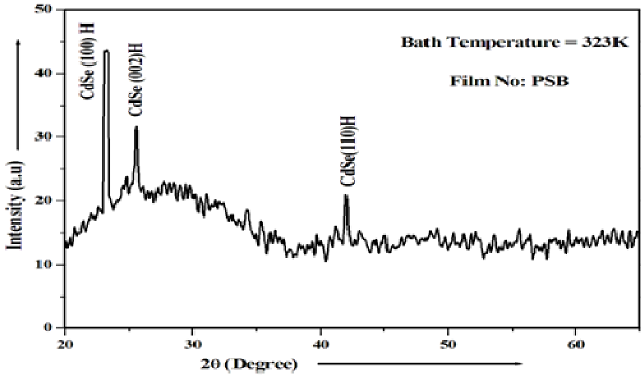

Figure 3. X-ray diffraction pattern of a CdSe film at a bath temperature 323K showing the hexagonal nature of the film (Film No. PSB)

Table 1. Structural Parameters of CdSe Thin Film (PSB) Prepared at Elevated Temperature

Film No.	Bath Temperature	2θ (Degree)	*hkl* planes	*d*-spacing in Å Standard	*d*-spacing in Å Observed	Lattice Parameter Å *c*	Lattice Parameter Å *a*	Crystallite Size (nm)	Dislocation Density (δ) x 10^{13} lines/ m^2
PSB	323K	23.17	(100)H	3.72	3.83				
		25.30	(002)H	3.50	3.48	6.98	4.309	13.4	5.569
		42.05	(110)H	2.14	2.14				

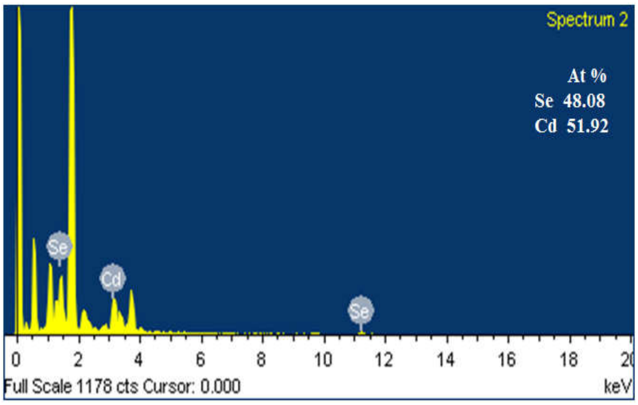

Figure 4. The EDAX spectrum of CdSe thin film deposited at 323K (Film No. PSB)

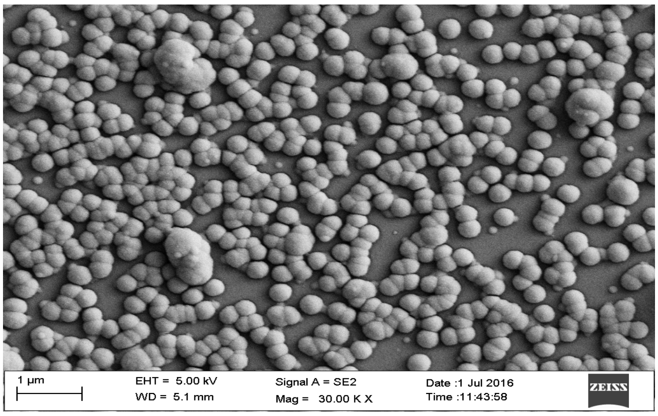

Figure 5. The SEM image of CdSe thin film deposited at 323K (Film No. PSB)

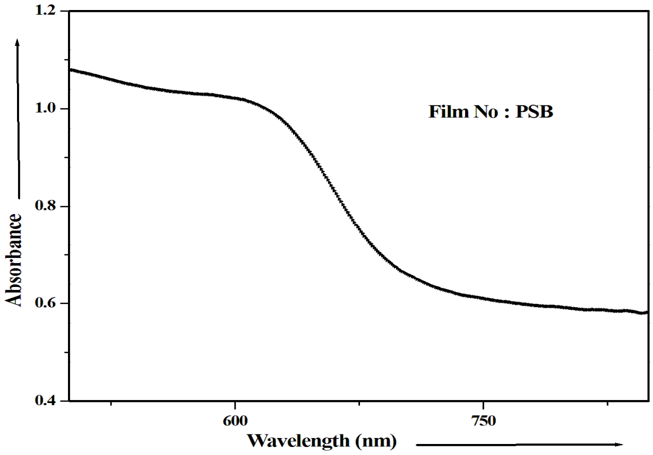

Figure 6. Plot of absorbance versus wavelength for CdSe thin film prepared at 323K

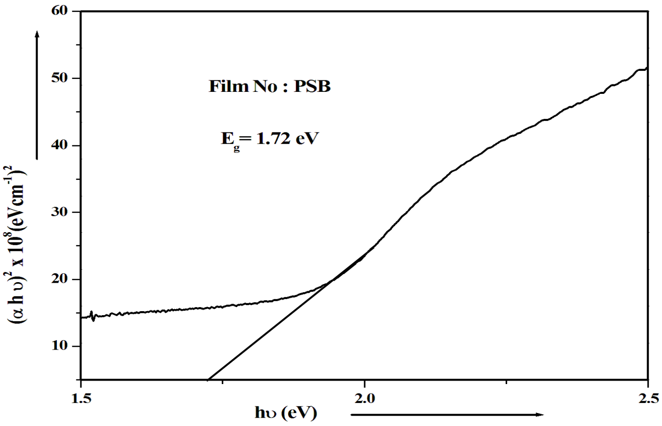

Figure 7. Plot of energy band gap $(\alpha h\nu)^2$ versus photon energy (hν) of CdSe thin film

Since the structure was hexagonal, the lattice constants *c* and *a* for the hexagonal phase, were calculated using the following relation (2.6):

$$1/d_{hkl}^2 = \frac{4}{3}[(h^2 + hk + k^2)/a^2] + (l/c)^2$$

Energy Dispersive X-Ray Analysis (EDX)

The quantitative analysis of the CdSe thin film was carried out by using EDAX method. The EDX spectra of CdSe thin film was shown in Figure 4. From EDX analysis, the average atomic percentage of Cd:Se was found to be 48.08:51.92 indicating that the film was in good stoichiometric ratio of the 'Cd' and 'Se'

Surface Morphology Analysis

Surface morphology study of CdSe thin film deposited at 323K was carried out with the help of scanning electron microscope (SEM). The SEM micrograph of the CdSe film was shown in Figure 5. The uniform surface morphology was observed over the entire glass substrate surface. The presence of fine grain background acquainted one-step growth by multiple nucleations. The SEM micrograph consisted of dense layer with some small crystallites. Some large particles were also embedded on the surface. Those particles were quite likely colloidal particles formed in the solution and adsorbed on the substrate during the growth of the film (Kale and Lokhande, 2000).

Optical Analysis

The optical properties were studied by using absorbance spectra for the CdSe thin film deposited on glass substrate at elevated temperature. The variation of optical absorbance with wavelength was shown in Figure 6. The study of optical absorption provided a simple way for explaining some features like the band structure. The optical absorbance spectrum of the as deposited CdSe thin film was analyzed at room temperature in the range of wavelength 200nm-1000 nm. From the Figure 6, it was clearly observed that for the as deposited thin film the absorption edge shifted towards a longer wavelength indicating red shift. The Tauc's equation was used to determine the band gap energy (E_g). Using Tauc's relation the direct band gap can be calculated by plotting $(\alpha h\nu)^2$ versus hν as shown in Figure 7. The plot was found to be linear which indicated the existence of direct transition. The calculated band gap value was 1.72 eV which was less than the bulk value. This decreased band gap value at elevated temperature was due to the increase in crystalline size and was also supported by the XRD results. In addition to the value was in good agreement with value reported earlier (Kale and Lokhande, 2000, Gudage *et al.*, 2009). The larger crystallite size with low transmission of stable hexagonal structure has special applications in photoelectrochemistry (PEC) and photovoltaic cells.

Conclusion

CdSe thin film had been synthesised by chemical bath deposition method, which is easy and low cost technique. CdSe film grows preferentially along c-direction with hexagonal structure at temperature 323K. The energy of band gap is lies within the ranges of semiconductor.

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