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Microstructural characterization of electro-deposited CdSe thin films

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Abstract: Thin films of CdSe were electrodeposited on tin oxide coated conducting glass substrates at various bath temperatures. The deposited films were characterized by x-ray diffraction (XRD) and scanning electron microscopy (SEM). X-ray diffraction studies revealed that the deposited films are found to be hexagonal structure with preferential orientation along (002) plane. The microstructural parameters such as crystallite size, R.M.S strain, dislocation density, stacking fault probability were calculated using x-ray line profile analysis technique. The variation of microstructural parameters with bath temperature and film thickness were studied and discussed.

1. Introduction

Thin films of II-VI group semiconductors are attracting a great deal of attention because of their various applications in photovoltaic, photodetection and optoelectronic devices [1-3]. Cadmium Selenide (CdSe) is an important material with a direct bandgap of 1.75 eV for the development of various modern technologies of solid state devices such as solar cells, high efficiency thin-film transistors, etc [4-5]. CdSe thin films are usually crystallized in hexagonal (wurtzite) structure [4], and in the cubic (zinc blende) structure [6]. Various deposition techniques such as pulsed laser deposition (PLD) [1], thermal evaporation [4], have been used for the preparation of CdSe films. Among these techniques, electrodeposition provide numerous advantages including low temperature growth, arbitrary substrate shapes, controllable film thickness, morphology and potentially low capital cost [7-8]. Most of the research reports on CdSe thin films dealt with the determination of structure type and qualitative observation of defects and grain size for CdSe thin films. A detailed quantitative measurement of different microstructural parameters and its dependence with bath temperature and film thickness for CdSe thin films on glass substrates obtained by thermal evaporation was reported earlier by Pal et al [9].

Quantitative study of different microstructural parameters and their dependence with bath temperature and film thickness for CdSe thin films coated on tin oxide coated conducting glass substrates have not been yet studied much for electrodeposited CdSe thin films. Knowledge of the microstructural analysis may provide valuable informations on the optimum growth conditions of the films. An x-ray diffraction study based on precise measurements upon the position broadening and shape of x-ray line profiles on polycrystalline thin film gives informations about the microstructural parameters which characterizes the microstructural variations in the films. The microstructural parameters such as crystallite size, R.M.S strain, dislocation density and stacking fault probability are found to influence the physico-chemical properties of electrodeposited CdSe thin films. Moreover, the reduction of stress, dislocation density and increase in crystallite size of CdSe thin films may be useful for opto-electronic applications. To our knowledge no report is available for microstructural characterization by x-ray line profile analysis for CdSe thin film growth by electrochemical route. In the present work, we describe the preparation of CdSe thin films on tin oxide coated conducting glass substrates by electrodeposition technique. X-ray line profile analysis technique by the method of variance has been used to evaluate the microstructural parameters such as crystallite size, R.M.S strain, dislocation density and stacking fault probability. The effects of bath temperature and film thickness on these microstructural parameters are studied and discussed.

2. Experimental Details

All the chemicals used in this work were of analytical reagent grade (procured from S.D Fine Chemicals, Mumbai, India).The electrodeposition of CdSe thin films on tin oxide coated conducting glass substrates were carried out in an aqueous electrolytic bath containing 250 mM $CdSO_4$ and 2.5 mM SeO_2 and the solution pH was maintained at 2.0 ± 0.1. The electrochemical experiments were performed using a PAR scanning potentiostat (Model 362, EG & G, Princeton Applied Research,USA) employing three electrode configuration with tin oxide coated conducting glass substrates as working electrode (sheet resistance 20 Ω/□), graphite plate as counter electrode and saturated calomel electrode (SCE) as a reference electrode, respectively. Before use, tin conductive oxide substrates were treated for 15 minutes with ultrasonic waves in a bath of isopropanol and then rinsed with acetone. The saturated calomel electrode was introduced into the solution by a luggin capillary whose tip was placed as close as possible to the working electrode. All the experimental potentials are referred to this electrode.

The cathodic potential at which the formation of single phase CdSe thin film occurs was found to be -700 mV Vs SCE. The plating experiments were carried out at various bath temperatures from 30 to 80^0C with different intervals of time. CdSe thin films were obtained under optimized conditions with good adherence to the substrates. Thickness of the deposited films was estimated using multiple beam interferometric and gravimetric method in the appropriate ranges. X-ray diffraction data of electrosynthesized CdSe thin films were recorded using an x-ray diffractometer (Philips Model PW 1710) with CuK_α radiation (λ= 0.15418 nm). Surface morphology of the films was analyzed using scanning electron microscope (Philips, Model XL 30).

3. Results and Discussion

X-ray diffraction patterns recorded for electrodeposited CdSe thin films on tin oxide coated conducting glass substrates with bath composition of 250 mM $CdSO_4$ and 2.5 mM SeO_2 at various bath temperatures from 30 to 80^0C are shown in Fig. 1.

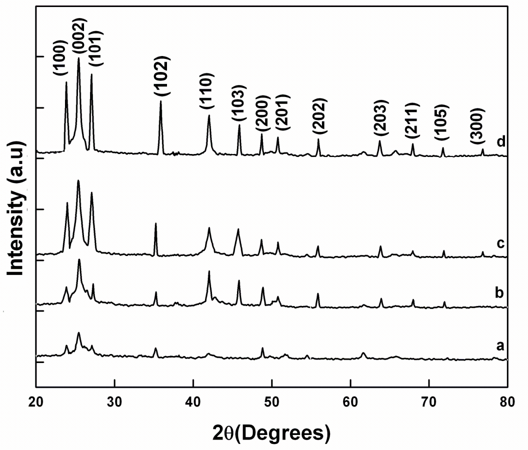

Fig. 1. X-ray diffraction pattern of CdSe thin films electrodeposited at various bath temperatures (a)30^0C (b)50^0C (c)70^0C (d)80^0C.

The observed diffraction peaks of CdSe are found at values of 23.87, 25.42, 27.07, 35.87, 42.02, 45.87, 48.72, 50.77, 55.92, 63.72, 67.92, 71.77 and 76.82 corresponding to the lattice planes (100), (002), (101), (102), (110), (103), (200), (201), (202), (203),(211),(105) and (300), respectively. X-ray diffraction studies revealed that the deposited films of CdSe are found to be polycrystalline in nature with hexagonal structure with lattice constants (a=4.299Å; c=7.010 Å). The different peaks in the diffractograms were indexed and the corresponding values of interplanar spacing "d" were calculated and compared with standard values [10]. It is observed from Fig. 1, that the height of the preferential peak increases and some new peaks of CdSe begin to appear while increasing bath temperature from 30 to 80^0C. It is also observed that the crystallites are preferentially oriented along (002) plane. For the calculation of crystallite size and strain the line profiles were subjected to variance analysis [11].An aggregate of distorted crystallites as a measure of the particle size and strain could affect the variance of the x-ray diffraction line profiles. Since the method is sensitive to the variation near the tails of the peaks, a careful adjustment of the background was carried out following the method of Mitra and Misra [12]. For instrumental broadening, the line profiles were corrected by substracting the variance of the corresponding profiles of well annealed CdSe samples, because of the additive effect of the variance. Assuming the broadening of the diffracted line is due to crystallite size and strain only, the variance can be written as

$$W_{2\theta}=\left[\frac{\lambda\sigma}{2\pi^{2}PCos\theta}\right]+\left[4\tan^{2}\theta<e^{2}>\right] \qquad (1)$$

where λ is the wavelength of x-rays used, σ the angular range over which the intensity distribution is appreciable, P the crystallite size and $<e^2>$ is the mean squared strain. Dislocation density is defined as the length of dislocation line per unit volume of the crystal given by Warren and Warekois [13]. Williamson and Smallman suggested one method to calculate the dislocation density as [14]

$$\rho=\left[\frac{(3nK/F)^{1/2}\ \langle e^{2}\rangle^{1/2}}{bP}\right] \qquad (2)$$

where P is the crystallite size, $<e^2>^{1/2}$ the R.M.S strain, b the Burgers vector, n the number of dislocations on each face of the particle, K the constant depending on the strain distribution and F is an interaction parameter. For Cauchy strain profiles the value of K is about 25, whereas for Gaussian strain profiles it is nearly 4. In the absence of extensive polygonization, dislocation density can be calculated from the above equation (2), by assuming n≈F, b=d, the interplanar spacing and K=4. Now the equation (2) reduces to

$$\rho = \frac{\sqrt{12}\langle e^2\rangle^{1/2}}{dP} \tag{3}$$

The stacking fault probability α is the fraction of layers undergoing stacking sequence faults in a given crystal and hence one fault is expected to be found in 1/ α layers. The presence of stacking faults gives rise to a shift in the peak positions of different reflections with respect to ideal positions of a fault-free, well-annealed sample. Four typical experimental profiles showing the peak shift for hexagonal (002) reflection of CdSe thin films at various bath temperatures with respect to a well-annealed bulk sample are shown in Fig. 2.

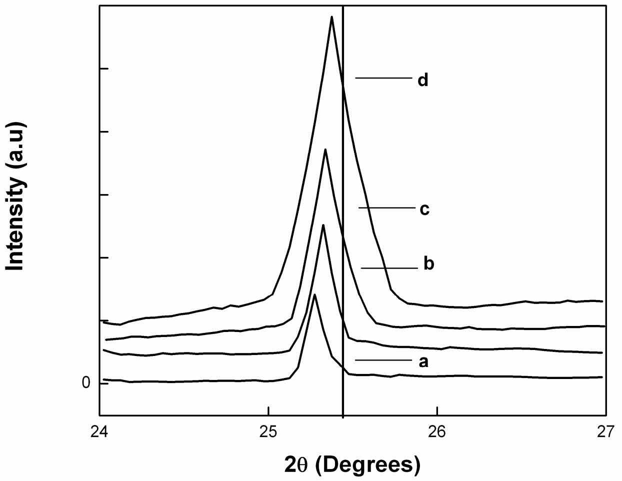

Fig.2. X-ray diffraction profile showing the peak shift and line broadening (a) 30^0C (b)50^0C (c)70^0C (d)80^0C.

A well-annealed powder sample reference is used to compare the shift in the peak position of different reflections and hence to evaluate the microstructural parameters. The relation connecting stacking fault probability (α) with peak shift Δ (2θ) was given by Warren and Warekois [14]. The stacking fault probability (α) is given by

$$\alpha = \left[\frac{2\pi^2}{45\sqrt{3}}\right]\left[\frac{\Delta(2\theta)}{\tan\theta_{002}}\right] \tag{4}$$

From the above expression (4) the stacking fault probability was calculated by measuring the peak shift with the well-annealed sample. The microstructural parameters such as crystallite size (P), R.M.S strain $<e^2>^{1/2}$, dislocation density (ρ) and stacking fault probability (α) were calculated.

Fig. 3 shows the variation of film thickness with bath temperature for films prepared at various bath temperatures. It is observed from Fig. 3 that the film thickness increases with bath temperature and attains its maximum value for films prepared at bath temperature of 80^0C.

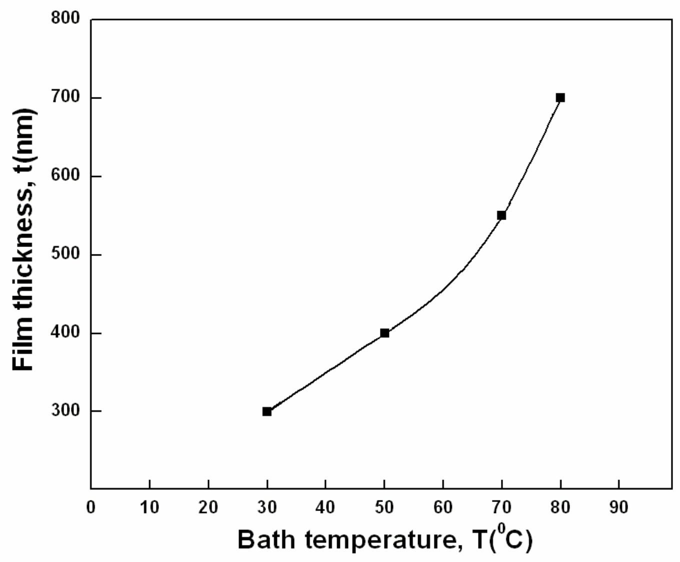

Fig. 3. Plot between bath temperature and film thickness.

The variation of crystallite size and R.M.S strain with film thickness for CdSe thin films electrodeposited at various bath temperatures from 30 to 80^0 are shown in Fig. 4.

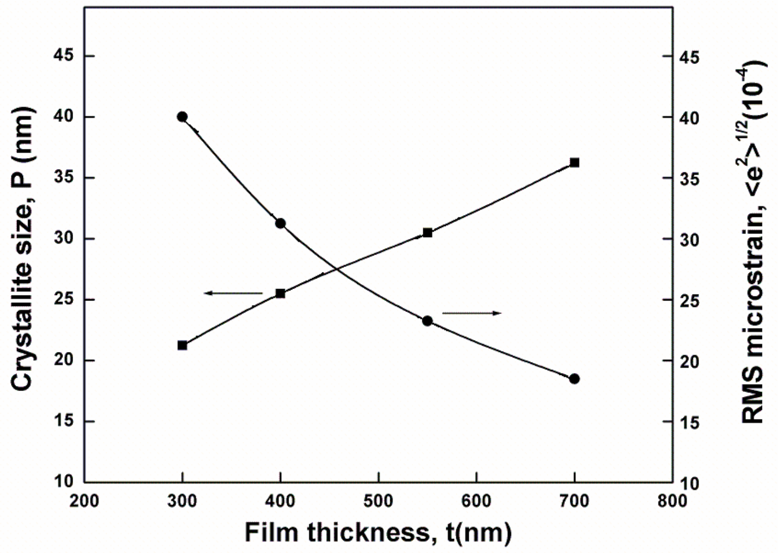

Fig. 4.Variation of crystallite size and R.M.S strain with film thickness for CdSe thin films.

It is observed from Fig. 4 that the film thickness increases the crystallite size increases and attained a maximum value for films prepared at 80^0C with thickness value of 700 nm. On the other hand the R.M.S strain decreases gradually with increase in film thickness and attained a minimum value for films prepared at 80^0C with film thickness of 700 nm. When the bath temperature increases, large number of Cd and Se ions gets adsorbed on the substrate which leads to crystallization. This effect is more predominant at higher bath temperatures which leads to a maximum value of crystallite size for films obtained at bath temperature of 80^0C which gives the maximum value of film thickness 700 nm. Due to the increase in crystallite size with bath temperature and film thickness, the defects in the lattice is reduced which in turn reduces the R.M.S strain. The variation of dislocation density and stacking fault probability with film thickness for films prepared at various bath temperatures is shown in Fig. 5.

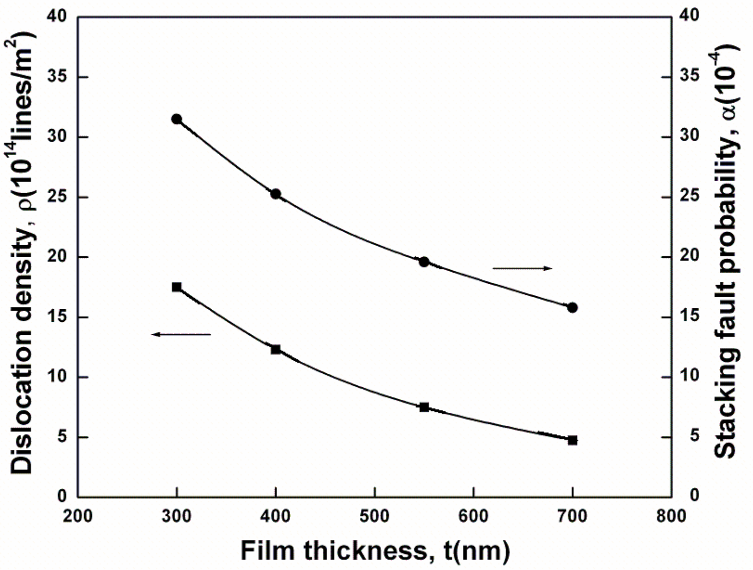

Fig.5. Variation of dislocation density and stacking fault probability with film thickness for CdSe thin films.

It is observed from Fig. 5, that the dislocation density and stacking fault probability are found to decreases with increase of bath temperature resulted increase in film thickness and minimum values are obtained for films prepared at bath temperature of 80^{0}C with film thickness of 700 nm. As the bath temperature increases, stresses in the layers and also the dislocation density decreases.

Due to the release of stresses build-up in the layers, the variation of interplanar spacing decreases which finally leads to a decrease in stacking fault probability for films deposited at a higher bath temperature of 80^{0}C. The studies on the effect of bath temperature and film thickness indicate that the R.M.S strain, dislocation density and stacking fault probability decreases with bath temperature and film thickness, whereas crystallite size increases. For thinner films, the R.M.S strain and hence the dislocation density are found to be larger. During the building up of film thickness the dislocation density and R.M.S strain are reduced due to the release of stress in the films. Also, with the increase of film thickness, the crystallite size increases gradually and tend to attain saturation for higher thicknesses.

The cumulative effect of decrease in the R.M.S strain value and dislocation density may be responsible for the gradual reduction in the stacking fault of the layers with increase in film thickness. Similar functional dependency of microstructural parameters on substrate temperature and film thickness for evaporated CdSe thin films have been reported earlier by Pal et al. [9].

The surface morphology of electrodeposited CdSe thin films was analyzed by scanning electron microscopy.

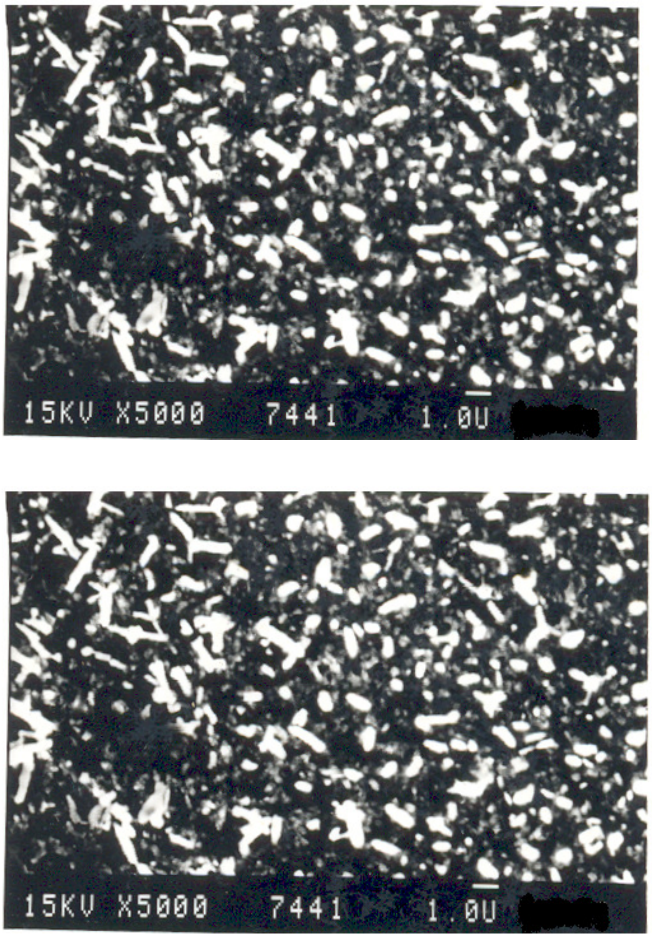

Fig. 6.a,b. SEM picture of CdSe thin films electrodeposited at different bath temperature (a)30^0C (b) 80^0C.

Fig. 6.a,b shows the SEM picture of CdSe thin films electrodeposited at bath temperature of 30 and 80^0C. It is observed from Fig. 6a that the film surface is found to be less uniform and covered with spherically shaped grains. Some pores and holes are seen at few places in the SEM picture. It is observed from Fig. 6b that the film surface is observed to be smooth, uniform and well covered with spherically shaped grains. The average sizes of the grains are found to be in the range between 0.4 and 0.5 µm. It can be concluded that the spherically shaped grains with uniform surface could be obtained for films prepared at higher bath temperature than those prepared at lower bath temperature.

4. Conclusion

Cathodic deposition of CdSe thin films on tin oxide coated conducting glass substrates have been carried out potentiostatically at various bath temperatures. The microstructural parameters for CdSe thin films were evaluated and the parameters are found to depend on film thickness and bath temperature. The R.M.S strain, dislocation density and stacking fault probability are found to decreases with increase in film thickness. The crystallite sizes of the films are observed to increase with increase in film thickness. It is observed that the microstructural parameters exhibit a monotonic variation with film thickness and bath temperature. The surface morphology reveals a substantial increase of grain size for films deposited at higher bath temperature.

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