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Electrosynthesis and Studies on CdZnSe Thin Films

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Abstract: *Electrodeposited CdZnSe thin films have been prepared at various bath temperatures. The thickness of the films was estimated between 850 nm and 1500 nm by stylus method. The X-ray diffraction patterns revealed that the electrodeposited CdZnSe alloy thin films are polycrystalline in nature with cubic structure. Microstructural properties such as, crystallite size, dislocation density, microstrain and number of crystallites per unit area were calculated using predominant orientation of the films. SEM images revealed that the surface morphology could be tailored suitably by adjusting the pH value during deposition. The surface roughness of the film was estimated using topographical studies. Optical properties of the film were analyzed from absorption and transmittance studies. Optical band gap of the films increased from 1.67 to 1.72 eV with the increase of bath temperature from 30 to 90^{o}C. The optical constants (refractive index (n) and extinction coefficient (k)) of CdZnSe thin films were evaluated using optical studies.*

Keywords: CdZnSe, Electrodeposition, Thin films, Optical properties

1. INTRODUCTION

Recently renewed interest in II–VI semiconductor materials is attributed to their wide spread use for the optoelectronic devices as well as solar cells fabrication process [1–3]. Zinc and cadmium chalcogenides are promising for improving II–VI semiconductor-based device performance. Namely, CdSe is a very promising candidate for photoelectrochemical cells and photoconductive cells, whereas ZnSe is a very important material for luminescent and light-emitting devices [4]. Nevertheless, CdSe is found to undergo photo corrosion when used in photoelectrochemical cells, whereas, ZnSe is reported to be more stable though less photoactive due to its wide bandgap [4–6]. To overcome this shortcoming, CdSe and ZnSe can be mixed so as to provide $Cd_{1-x}Zn_xSe$ ternary alloys.The importance of these materials lies in the fact that their energy band gaps and lattice parameter can be tailored independently which can lead to new semiconductor materials that may be suitable for accomplishing the twin tasks of increased absorption of solar spectrum and enhanced resistance towards photo corrosion [4,7,8]. Owing to the composition dependent properties of ternary alloys, $Cd_{1-x}Zn_xSe$ have attracted much attention in the fields of opto electronic and photoelectrochemical solar cell devices because of its wide optical band-gap and good stability with respect to environment [9–11]. In fact, the zinc concentration in $Cd_{1-x}Zn_xSe$ thin films plays important role for the high performance of photoelectrochemical solar cells [11]. Experimentally, thin films of $Cd_{1-x}Zn_xSe$ have been fabricated by vacuum evaporation [12], molecular beam epitaxy [13], electron beam pumping [14], chemical bath deposition [10,15,16], etc.

In the present work, thin films of CdZnSe are electrodeposited on indium doped tin oxide (ITO) coated conducting glass substrates by potentiostatic electrodeposition technique from an aqueous electrolytic bath. The deposited films are characterized using X-ray diffraction, Scanning electron microscopy, atomic force microscopy, Energy dispersive analysis by X-rays and Optical absorption techniques, respectively. The effect of bath temperature on structural, morphological, compositional and optical properties of the films are studied and the results are discussed.

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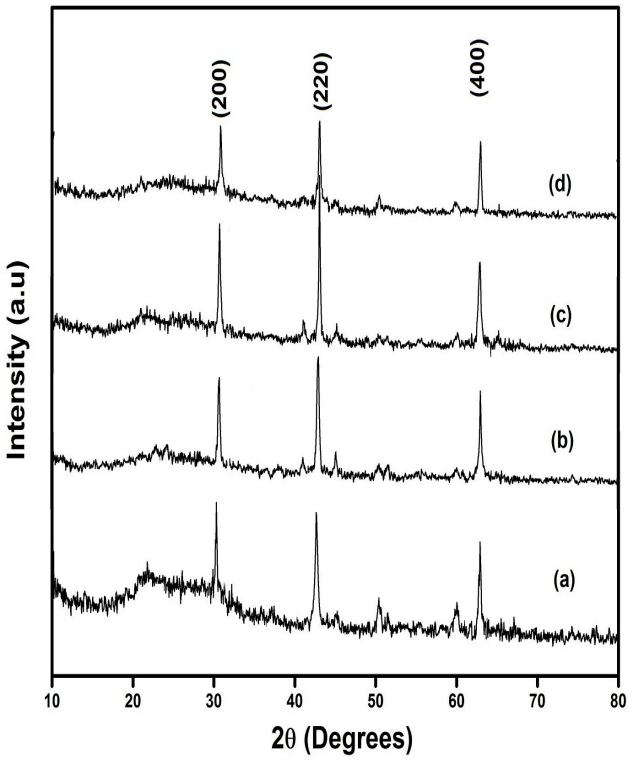

Figure 1. X-ray diffraction patterns of CdZnSe thin films electrodeposited at various bath temperatures: (a) 30° C (b) 50°C (c) 70°C and (d) 90° C.

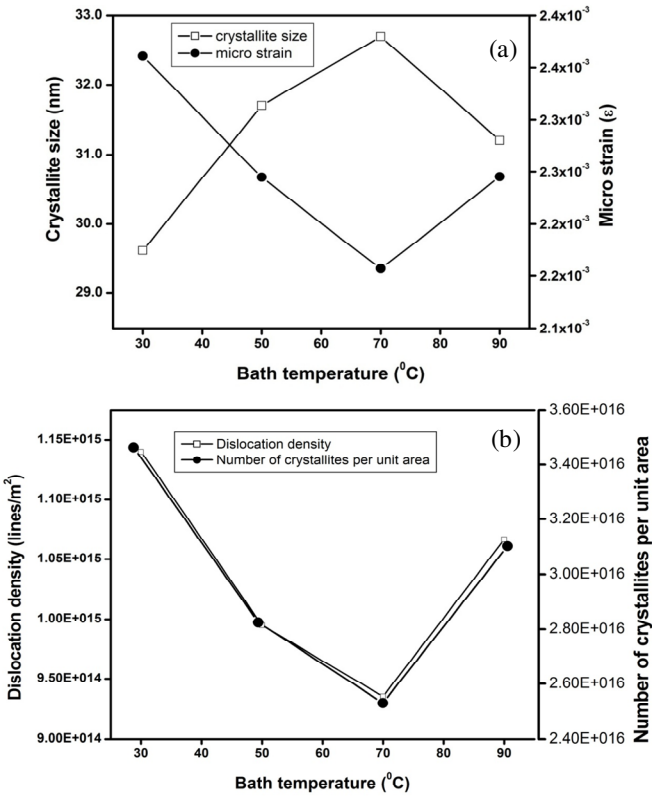

Figure 2. Microstructural properties of CdZnSe thin films for various bath temperatures (a) crystallite size and strain (b) dislocation density and number of crystallites per unit area

2. EXPERIMENT DETAILS

CdZnSe thin films were grown by electrodeposition technique using potentiostatic method. The deposition process depends on various parameters such as deposition potential, bath temperature, solution pH and electrolyte concentration. A standard three electrode cell was used for the electrodeposition CdZnSe. Indium doped tin oxide (ITO) was used as working electrode, graphite rod as counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. ITO coated glass substrates were first cleaned in acetone, and thoroughly rinsed with distilled water. The deposition of CdZnSe thin films was carried out from an aqueous electrolyte containing 0.03 M, 0.01M and 0.005M concentrations of $CdSO_4$, $ZnSO_4$ and SeO_2 at a deposition potential is -750mV vs SCE. The solution pH was adjusted to 2.5 by the addition of H_2SO_4 solution. The deposition bath temperature was varied from 30°C to 90°C and CdZnSe thin films were deposited.

Electrodeposition was carried out using an electrochemical system consisting of PAR (EG&G Princeton Applied Research, USA Model 362A) potentiostat/galvanostat unit. Thickness of the deposited films was measured using stylus profilometer (Mitutoyo SJ 301). An X-ray diffractometer system [X'PERT PRO PANalytical, Netherlands] with Cuk_α radiation (λ = 0.1540) nm was used to identify the crystal structure of the films. A surface morphological study was carried out using a scanning electron microscopy (Philips Model XL 30, USA). Model DSR-XE-100^{TM} atomic force microscopy has been used for the surface analysis of CdZnSe thin films. Optical properties of the samples were analyzed using a UV-Vis- NIR double beam spectrophotometer (HR - 2000, M/S ocean optics, USA).

3. RESULTS AND DISCUSSION

The structural properties of electrodeposited CdZnSe thin films was investigated by X-ray diffraction using Cuk_α radiation with λ = 0.154 nm. Figure 2 shows typical X-ray diffractogram of CdZnSe films deposited at various bath temperatures such as 30°C, 50°C, 70°C and 90°C grown on ITO substrates. X-ray diffraction studies reveal that as-deposited films are polycrystalline in nature and belong to the cubic phase with a preferential orientation along (220) direction. The (220) peak position is located at 2θ = 43.3 corresponding to the lattice parameter value 0.583 nm, for films grown at various bath temperatures. The composition of films changes considerably for samples deposited at potential -750 mV vs SCE deposited at various bath temperatures. It is found that when the bath temperature is increased up to 70°C the intensity of cubic peak is also increased. At higher bath temperature (90°C) was the intensity of the predominant peak decreased for the CdZnSe cubic phase were observed in the X-ray diffraction patterns. The observed peaks in the diffraction patterns were indexed and the corresponding values of lattice spacing "d" were calculated and compared

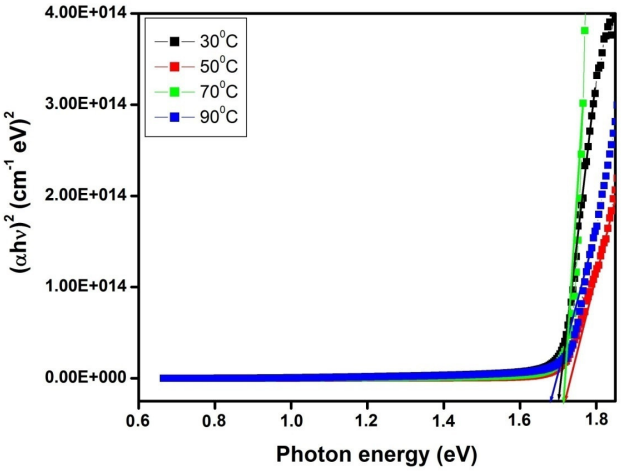

Figure 3. Plot of hν versus $(\alpha h\nu)^2$ for CdZnSe thin films electrodeposited at various bath temperatures

with JCPDS standards [17]. All the peaks identified are from CdZnSe and hence no additional lines corresponding to individual elements of Cd, Zn and Se are present. This observation reveals that electrodeposition method is suitable for obtaining polycrystalline CdZnSe thin films.

The crystallite size D of the films was calculated from the Debye Scherer's formula from the full-width at half-maximum intensity (FWHM) expressed in radians.

$$D = 0.9\lambda / \beta \cos\theta \tag{1}$$

where D is crystallite size and β is the FWHM. From (hkl) planes, the The origin of the micro strain is related to the lattice misfit, which in turn depends upon the deposition conditions. The crystallite size and micro strain for the electrodeposited CdZnSe films were obtained from full width at half maximum which can be expressed as linear combination of contributes from the particle size, D and strain ε given below. The micro strain ε is calculated using the relation,

$$\frac{\beta \cos\theta}{\lambda} = \frac{1}{D} + \frac{\varepsilon \sin\theta}{\lambda} \tag{2}$$

where λ is wavelength, D is crystallite size, β is FWHM of the predominant orientation and θ is Bragg's angle. It was also evident from X-ray diffraction patterns of CdZnSe thin films deposited at various bath temperatures between 30 and 90^0C were recorded. Using FWHM method and Debye–Scherrer equation, the crystallite size of the films were calculated. The variation of crystallite size and micro strain with bath temperature for CdZnSe film is shown in Figure 4a. X-ray line profile analysis revealed that the crystallite size increases with bath temperature and the films deposited at 70^0 C are found to have maximum value of crystallite size. Due to the removal of defects in the lattice with increase in bath temperature the micro strain in the films get released and attained a minimum value at 70^0C. A sharp increase in crystallite size and decrease in

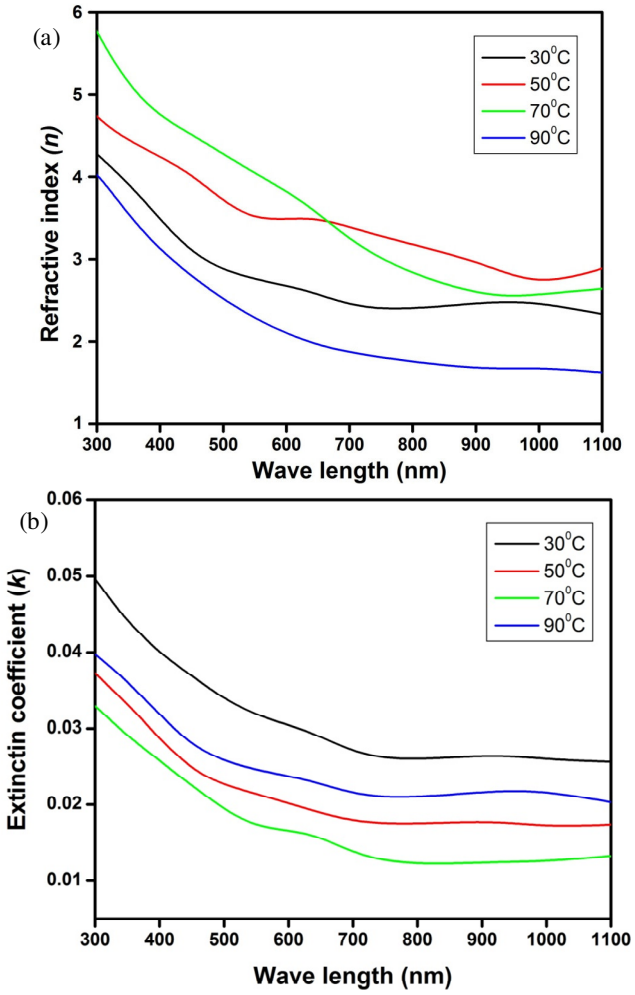

Figure 4. (a) Variation of refractive index (n) and (b) extinction coefficient (k) as a function of wavelength (λ) for CdZnSe thin films obtained at various bath temperatures.

micro strain with bath temperature is shown in figure 4a.

The dislocation density δ defined as the length of dislocation lines per unit volume of the crystal and can be evaluated from the particle size D by the relation:

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

where n is a factor, when equal unity giving minimum dislocation density. The number of crystallites per unit area (N) of the films was determined with the using formula,

$$N = \frac{t}{D^3} \tag{4}$$

where t is thickness of the film, N number of crystallites per unit area and D crystallite size. Such release in micro strain reduced the variation of interplanar spacing and thus leads to decrease in dislo-

Figure 5. SEM picture of CdZnSe thin film obtained at bath temperature 70° C.

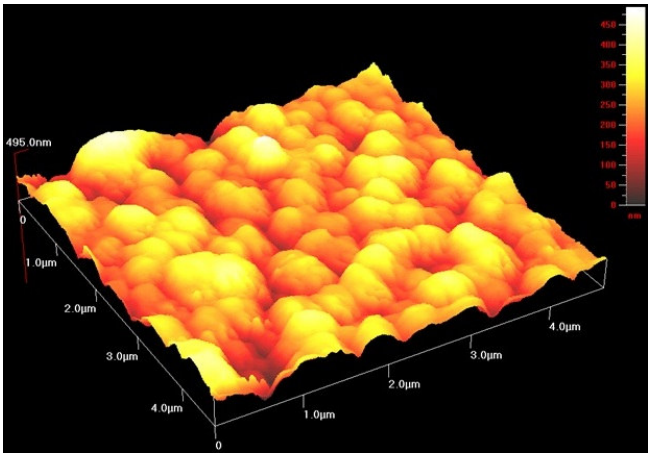

Figure 6. AFM image of CdZnSe thin film obtained at bath temperature 70° C.

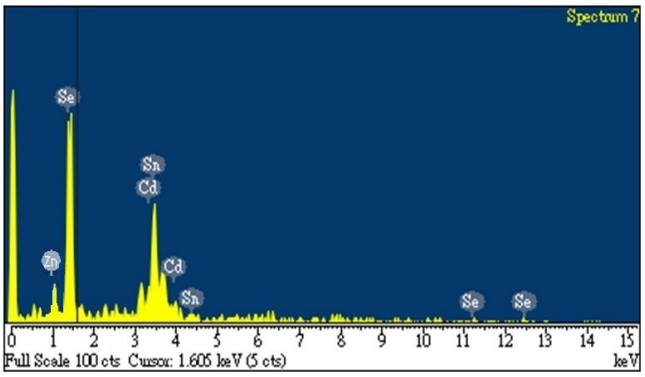

Figure 7. Typical EDX spectrum of CdZnSe thin film obtained at bath temperature 70° C.

cation density and number of crystallites per unit area of the film (Figure 4b) and minimum values are obtained for films deposited at 70^0 C. CdZnSe films with lower micro strain, dislocation density and number of crystallites per unit area improves the stoichiometry of the films which in turn causes the volumetric expansion of thin films. The polycrystalline nature of CdZnSe film is due to the presence of Se ion vacancies within the lattice. Crystallinity improvements with bath temperature enhance the concentration and mobility of Se ion vacancies within the lattice and hence reduce the resistivity of the films. The studies on functional dependency of microstructural parameters on bath temperature indicate that the micro strain, dislocation density, number of crystallites per unit area decreases with bath temperature whereas the crystallite size increases.

The optical parameters such as absorption coefficient and band gap are determined from optical absorption measurements. The value of absorption coefficient for strong absorption region of thin film is calculated using the following equation (9) [18],

$$\alpha = \frac{1}{t}\ln\left(\frac{A}{T}\right) \tag{5}$$

where α is the absorption coefficient in cm^{-1}, t is the thickness of the films, A is absorbance and T is transmittance. The nature of transition is determined using the following equation (10) [18],

$$\alpha h\nu = A\left(h\nu - E_g\right)^n \tag{6}$$

Optical transmission spectra were recorded at room temperature in air to obtain information on the optical properties of CdZnSe thin films. The optical absorption data is used to plot a graph of $(\alpha h\nu)^2$ versus $h\nu$, where α is the optical absorption coefficient of the material and $h\nu$ is the photon energy. Extrapolation of the plots to the *x*-axis gives the band gap energy of the CdZnSe film deposited at 30 - 90^0C (Fig. 6). The band gap energy of CdZnSe thin film deposited at various bath temperatures in the range of 1.67 -1.72 eV and this value is in good agreement with the value reported earlier. Transmission spectrum is used to calculate the refractive index using the envelope method proposed by Swanepoel [19,20].

$$n = \left[N_1 + \left(N_1^2 + s^2\right)^{1/2}\right]^{1/2} \tag{7}$$

$$N_1 = 2s\frac{T_M - T_m}{T_M T_m} + \frac{\left(s^2+1\right)}{2} \tag{8}$$

T_M and T_m are the values of maximum and minimum transmission values at a particular wavelength, '*s*' is the refractive index of the substrate. Refractive index can be estimated by extrapolating envelops corresponding to T_M and T_m. These fringes can be used to calculate the refractive index (*n*) of the thin films using equations (11) & (12). The refractive index corresponding to T_M and T_m for same wavelengths are calculated. The variation of refractive index with wave length of incident radiation for CdZnSe thin films is shown in Fig. 7. Refractive index found to decrease with the wave length of the film. It is also seen in figure that the refractive index

significantly depends on thickness of the films. It is evaluated that in the refractive index spectra, the lower thickness films exhibit a higher energy region, while the higher thickness films exhibit a lower energy region. The extinction coefficient can be calculated by using the relation [21].

$$k = \frac{\alpha\lambda}{4\pi} \tag{9}$$

where α is absorption coefficient, λ is wave length and R is reflectance of the CdZnSe thin films. The refractive index and extinction coefficient of the thin films are estimated from following equations (7) and (9). Fig. 7 show the refractive index, n, and the extinction coefficient, k, respectively, for electrodeposited CdZnSe thin film as a function of wavelength. It is obvious that a remarkable variation is observed in both n and k values. The refractive index is found to decrease with increase in wavelength of the incident photon. At higher wavelength of the incident photon, the refractive index tends to be constant [22].

However, in figure 5 the SEM micrograph obtained at optimized bath temperature (70°C) reveals a surface uniformly constituted. It is observed in figure 5 that the surface homogeneity of the films is improved. It is also observed that small grains agglomerate to form larger grains. The surface is covered well with more number of spherical grains. The grain sizes of CdZnSe thin film covered the entire surface of the film are estimated to be in the range between 100 and 150 nm. When the bath temperature is 70°C, more grain growth occur, thereby the average grain size is increased due to agglomeration of smaller grains together. It is evident that by altering the bath temperature the surface features may be modified. When the bath temperature is decreased, the surface mobility is increased. This is turn allows the films to lower its total energy by grain growth and decrease in the grain boundary areas.

Atomic force microscope studies reveal smaller grains on the surface of the CdZnSe thin film grown 70°C as shown in figure 6. However, larger grains were observed on the surface of the films deposited at bath temperature 70°C. Atomic force microscope studies exhibit the formation of uniform CdZnSe thin films with average size of 150 nm. AFM reveals the granular nature of particles and agglomeration of particles is seen from the 3D micrographs. The root mean square value of the surface roughness of the film from different areas of the film is calculated. The roughness of the films was also measured by atomic force microscopy (AFM) using Ra values, and we observed a strong dependence of the roughness on the different bath temperature. It is found that the surface roughness of electrodeposited CdZnSe thin film is 25 nm. It is estimated that 25% increase in surface roughness is found for films deposited at bath temperature 70°C than these deposited at low bath temperatures. Grain size of the films increases with bath temperature and in turn the surface roughness also increases with bath temperature. Similar behaviour was reported earlier for chemical bath deposited bismuth selenide thin films [23].

The presence of elemental constituents is confirmed from EDAX analysis. The average atomic percentage ratio of CdZnSe is found to be 1:1:1 is as shown in figure 8. The low bath temperatures the film stoichiometry formation is slightly changed. In this feature is also observed in the structural studies for its diffraction peaks of CdZnSe thin films. But the higher bath temperature the film is observed high Zn content and low Cd content and also revealed its corresponding diffraction patters.

4. CONCLUSIONS

Thin films of CdZnSe were deposited on indium doped tin oxide coated conducting glass substrates using potentiostatic electrodeposition technique. X-ray diffraction studies reveal that deposited films are exhibit polycrystalline cubic structure with preferential orientation along (220) plane. No phase transformation is observed for films prepared at various bath temperatures. The structural parameters such as crystallite size, microstrain, dislocation density and number of crystallites per unit area are evaluated and their properties change its deposition bath temperature. The bath temperature was optimized as 70° C on the basis of structural studies and film stoichiometry. SEM observation shows that smooth surface with spherically shaped grains obtained at bath temperature 70°C. The band gap of CdZnSe thin films obtained at optimized condition in the present work is found to be 1.70 eV which is quite closer to the value reported earlier. The refractive index and extinction coefficient values are very good response for device fabrications.

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