Journal of New Materials for Electrochemical Systems 15, 43-48 (2012)
© J. New Mat. Electrochem. Systems

Annealing Effects on the Properties of Electrodeposited CdSSe Thin Films

T. Mahalingam[1,*], V. Dhanasekaran[1], S. Rajendran[1], G. Ravi[1], Luis Ixtlilco[2] and P.J. Sebastian[3]

[1]Department of Physics, Alagappa University, Karaikudi - 630 003, India.
[2]Universidad Politécnica del Estado de Guerrero, Carretera Taxco-Iguala, Ejido de Arroyo s/n, CP. 40290, Taxco, Guerrero, México
[3]Solar-Hydrogen-Fuel Cell Group, CIE-UNAM, Temixco 62580, Morelos, Mexico

Received: June 17, 2011, Accepted: September 20, 2011, Available online: December 06, 2011

Abstract: *The effect of post heat treatment on structural, morphological and optical properties of electrodeposited CdSSe solid solution thin films were studied using X-ray diffractometer (XRD), scanning electron microscopy (SEM), and UV-Vis-NIR spectrophotometer, respectively. X-ray diffraction patterns revealed that polycrystalline nature with hexagonal structure of CdSSe thin films. Also the microstructural properties are calculated tends to increase and the face centred hexagonal orientation of CdSSe thin film is enhanced significantly by increasing the annealing temperature. Scanning electron microscopic images revealed that the hexagonal shaped grains are occupying the entire surface of the film. The optical transmittance and absorption spectra were recorded in the range 400 to1100 nm. The band gap of the CdSSe thin films was found to decrease from 2.0 eV to 1.8 eV due to annealing temperature. The real part of the complex refractive index (n) and the imaginary part extinction coefficient (k) were calculated before and after annealing.*

Keywords: Thin films, Electrodeposition, CdSSe, Semiconductor

1. INTRODUCTION

Cadmium sulphoselenide (CdSSe) is a ternary chalcogenide semiconductor whose bandgap varies from 1.7 eV (CdSe) to 2.5 eV (CdS). It is widely used as a semiconducting material, mainly as photoconductors, but with increasing interest focused on their use in photovoltaic and photoelectrochemical (PEC) devices. [1]. CdSSe is photoconducting material sensitive to the visible wavelength of light. Vapour phase crystal growth of CdSSe has been carried out [2]. CdS,CdSe system in the entire range of X has the same crystal structure and type of conductivity. For many applications, thin layer of CdSSe on sub strates are normally required. There are many methods of preparing sucha thin films, such as by evaporation, CVD, spray pyrolysis and electrochemical deposition. CdSSe thin films from aqueous medium have been electrodeposited and used in PEC cells. It was observed that Se incorporation in CdS lowers ithe bandgap energy, Eg of CdS material and enhances its photoelectrochemical solar cell conversion efficiency [3]. Literature survey showed that very little work has been reported on the preparation of CdSSe thin films by chemical method [4-5]. In recent years, a lot of work on $CdS_{1-x}Se_x$ focused on the dynamical properties of localized excitons because they represent a model system for fundamental studies, concerning the effect of disorder on the carrier dynamics. The well-known phenomenon of disorder-induced exciton localization has also been observed in other II-VI and III-V solid solutions [6-8]. Mane et al [9] have reported the optical properties showed that Se incorporation in CdS film decreases the optical bandgap. All the films deposited by chemical bath deposition are n-type and semiconducting evidenced by electrical measurement studies.

In the present study, we report the annealing effect of electrodeposited CdSSe solid solution thin films on indium tin oxide (ITO) coated glass substrates by potentiostatic mode. The structural, morphological and optical properties of the prepared thin films in as-deposited condition were studied using X-ray diffraction, scanning electron microscopy (SEM) and optical absorption techniques.

2. EXPERIMENT DETAILS

CdSSe thin films were grown by electrodeposition technique using potentiostatic method. The deposition process depends on various parameters such as deposition potential, bath temperature,

---

*To whom correspondence should be addressed: Email: maha51@rediffmail.com
Phone: +91 4565 230251

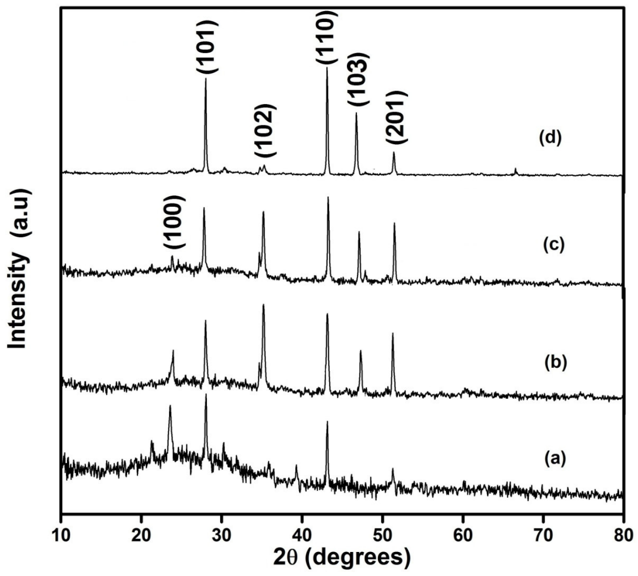

Figure 1. X-ray diffraction patterns of electrodeposited CdSSe thin films (a) un anneal (b) 200°C (c) 300°C and (d) 400°C.

solution pH and electrolyte concentration. A standard three electrode cell was used for the electrodeposition CdSSe. 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 electrodeposition of CdSSe was carried out cathodically from an aqueous bath composed of $CdSO_4$, $Na_2S_2O_3$ and SeO_2.. The deposition of CdSSe thin films was carried out from an aqueous electrolyte containing 0.02 M, 0.1 M and 0.002M concentrations of $CdSO_4$, $Na_2S_2O_3$ and SeO_2 at a deposition potential and bath temperature are -750mV vs SCE and 75°C, respectively. The solution pH was adjusted to 3.0 ± 0.1 by the addition of H_2SO_4 solution. For air annealing the samples a furnace is employed. The post annealing temperatures and time were selected by the stability of the samples.

Electrodeposition was carried out using an electrochemical system consisting of PAR (EG&G Princeton Applied Research, USA Model 362A) potentiostat/galvanostat unit. An X-ray diffractometer system [X'PERT PRO PANalytical, Netherlands] with Cuk$_\alpha$ radiation (λ = 0.1540) nm was used to identify the crystal structure of the films. Surface morphological was carried out using a scanning electron microscopy (Philips Model XL 30, USA). 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

Figure 1 shows the XRD patterns of the CdSSe thin films unanneal and various annealing temperatures such as 200°C, 300°C and 400°C. The '*d*" (interplanar spacings) values of the XRD reflections were compared with standard '*d*" values taken from JCPDS diffraction file (No. 50-0721). The observed good agreement d values are very good agreement with standard *d*' values and it is represent that films are deposited primitive hexagonal phase with (110) crystallographic orientation. Annealing the films at 200° C , 300°C and 400° C for 60 min in air produces a considerable improvement in crystallinity, showing more intense and sharper XRD peaks. The interpretation of the X-ray diffraction pattern of the 800 nm thick CdSSe film on conducting glass substrates (Fig. 1) shows that it is exhibit polycrystalline in nature hexagonal crystal structure. The highest peak at angle $2\theta = 43.51^0$ corresponds to the (110) reflection, the other peaks are at angles 24.30, 27.521, 34.98, 48.10 and 51.70 and corresponding to the crystallographic planes (100) (101) (102) (103) and (201), respectively. The large peak at 43.51^0 indicates that CdSSe thin film is preferentially oriented along the (101) plane. An increase of annealing temperature in the CdSSe films sharpened the (110) peak. It can be seen that there is sharp and strong peaks observed in all patterns. When annealing the samples some new peaks are appeared also broadening of the predominant peak decrease it may be due increase crystallinity of the samples. But (100) plane intensity decrease when increase annealing temperature till 200^0C, hereafter increase annealing temperature in this peak has been disappeared. The post heat treatment is affect only the crystallinity and microstructure of the film but no phase transformation take place. Similar findings were also reported by other authors [10,11]. This suggests that the annealing process of the investigated system brought about a progressive increase in the degree of crystallinity of CdSSe hexagonal phases and led to a progressive increase in their grain size. There is very good changes occur in the annealing x-ray diffraction pattern when compared in as-deposited films.

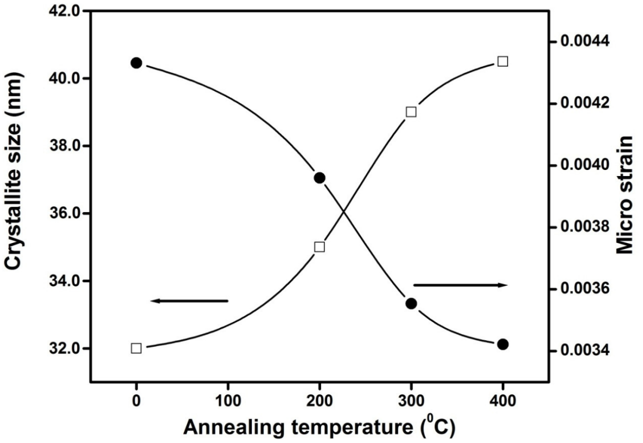

Figure 2. Crystallite size and micro strain with various annealing temperatures for CdSSe thin films.

Figure 2 shows that calculated crystallite size and micro strain with their corresponding annealing temperatures. The crystallite size D of the films was calculated from the Debye-Scherer's [12] formula from the full-width at half-maximum intensity (FWHM) expressed in radians, using the formula $D = [0.9\lambda/\beta\cos\theta]$,where D is crystallite size and β is the FWHM. The larger full-width at half-maximum (FWHM) observed for unannealed CdSSe films made of nanocrystallites. When increase annealing temperature the film as increase crystallite size shown figure. Because post heat treatment to grow the crystallite of its thermal expansion properties. X-ray

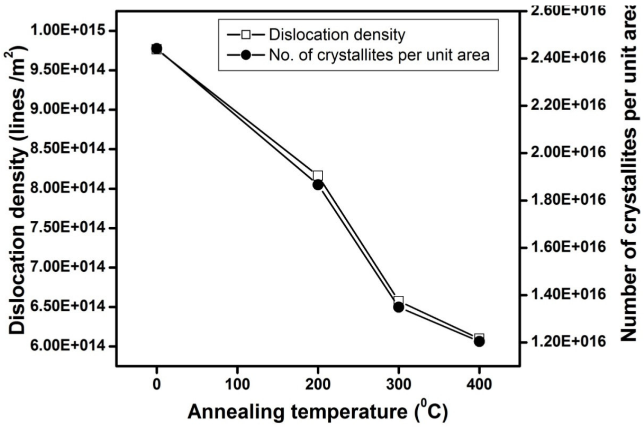

Figure 3. Dislocation density and number of crystallites per unit area with various annealing temperatures for CdSSe thin films.

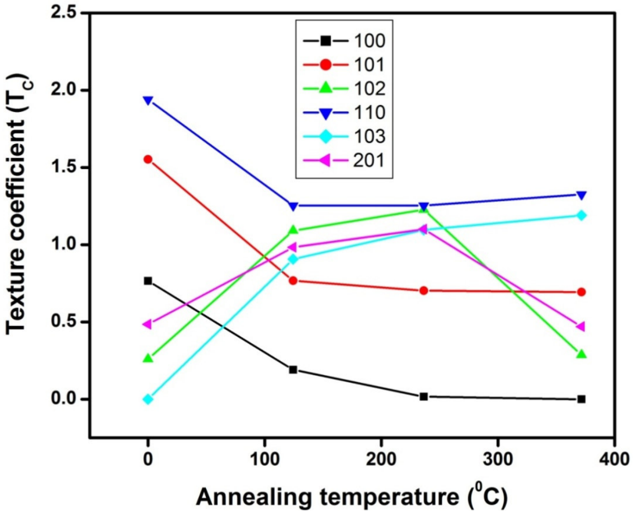

Figure 4. Texture coefficient with various annealing temperatures for CdSSe thin films.

line profile analysis revealed that the crystallite size increases with annealing temperature and the films are found to have maximum value of crystallite size in 40.5 nm. Due to the removal of defects in the lattice with increase in annealing temperature the microstrain in the films get released and attained a minimum value at 400^{0}C. The calculated crystallite size is range between 32 and 40.5 nm.

The calculated crystallite size of the film and their corresponding micro strain (ε) is estimated. The microstrain (ε) is calculated using the relation [13].

$$\varepsilon = \frac{\lambda}{D Cos\,\theta} - \frac{\beta}{Tan\,\theta} \tag{1}$$

A sharp increase in crystallite size and decrease in microstrain with annealing temperature is shown in Figure 3. Such release in microstrain reduced the variation of interplanar spacing and thus leads to increase in crystallite size and minimum values are obtained for films annealed at 400^{o}C.

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:

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

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,

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

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 dislocation density and number of crystallites per unit area of the film (Figure 3) and minimum values are obtained for films deposited at maximum annealing temperature. CdSSe 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 CdSSe solid solution thin film is due to the presence of Se ion vacancies within the lattice. Crystallinity improvements with deposition potential 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 micro structural parameters on CdSSe thin films indicate that the micro strain, dislocation density, number of crystallites per unit area increases with deposition potential whereas the crystallite size decreases.

The texture coefficient was calculated using an expression,

$$T_C(h_ik_il_i) = \frac{I(h_ik_il_i)}{I_0(h_ik_il_i)}\left[\frac{1}{n}\Sigma\frac{I(h_ik_il_i)}{I_0(h_ik_il_i)}\right]^{-1} \tag{4}$$

where I_0 represents the standard intensity, I is the observed intensity of *($h_ik_il_i$)* plane and n is the reflection number. The crystallite shape of the cadmium sulfoselenide film is strongly related to the texture coefficient of the film. The texture coefficient of different lattice planes of CdSSe thin films are shown in Figure 4. The predominant plane orientation of the film has high texture coefficient value. Also annealing temperature increase the texture coefficient value is decreases it may be owing to some new peaks are appeared. Because of this changes may be due to the some new crystallographic oriented peaks are emerged also peak intensity is increased. It has been reported for copper oxide film [14] earlier that texture coefficient is higher than 1 indicates preferential orientation and also indicates the abundance of grains in a given (h_i,k_i,l_i) direction.

Figure 5 shows the transmittance of un annealed and 400^{0}C annealed CdSSe thin films. The un annealed films have a transmittance in the visible of 55% and annealed sample increases the transmittance in the visible to 75%. The increase in the transmittance is due to an increase in the band gap with carrier concentra-

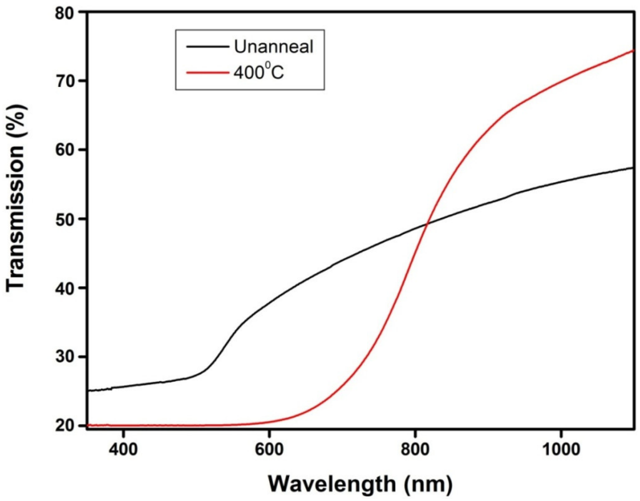

Figure 5. Optical transmission spectra of unanneal and maximum annealing temperature(400°C) for CdSSe thin films.

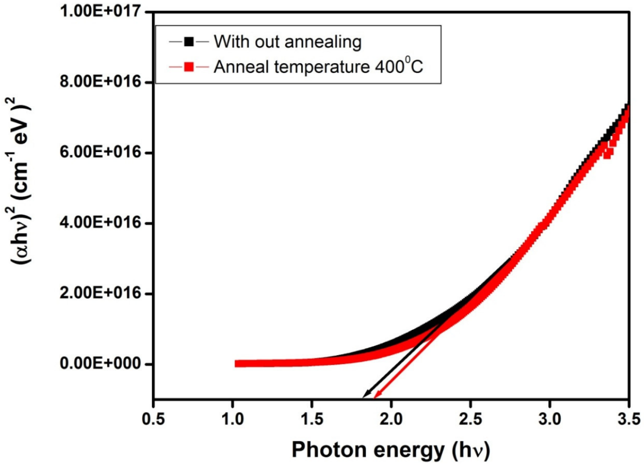

Figure 6. Plot of hν vs $(\alpha h\nu)^2$ of un anneal and maximum annealing temperature (400°C) for CdSSe thin films.

tion. To study the optical properties of the materials, the transmittance versus the photon energy of the CdSSe was determined. The nature of transition is determined using the following equation (2) [15],

$$\alpha h\nu = A\left(h\nu - E_g\right)^n \tag{5}$$

where α is absorption coefficient in cm^{-1} , hν is photon energy, Eg is an energy gap, A is energy dependent constant and n is an integer depending on the nature of electronic transitions. For the direct allowed transitions, n has a value of 1/ 2 while for indirect allowed transitions, n = 2.

The band gap energy of the grown thin films can be determined by extrapolation of the linear part of the plot of $(\alpha h\nu)^2$ versus the incident radiation energy, *hv* , as shown in Figure 6; which indicates that the near band edge optical absorption coefficient has spectral dependence of only the joint density of states in samples. The optical absorption edge has been observed at a wavelength of about 685 nm corresponding to band gap energy of about 1.81 eV for non- annealed sample. This value is quite consistent with the literature for as-deposited CdSSe films grown [16]. The observed band gap energy of the annealed sample is about 1.89 eV corresponding to a wavelength of 656 nm. These results show that the band gap energy of CdSSe thin film shifts to higher energy values after annealing. The increase of the band gap energy after annealing is quite consistent with some of the following studies in the literature for various thin films. For example, Bouhssira et al. have shown that the ZnO band gap energy increases from 3.3 eV in as-grown up to 3.7 eV after systematic annealing experiments at temperatures from 100 to 600^0 C [17]. They attribute the blue shift of the optical absorption edge to the increasing crystallinity quality of the CdSSe films. Most of these films are on much larger substrates in terms of melting point such as sapphire so that they can anneal at higher temperatures.

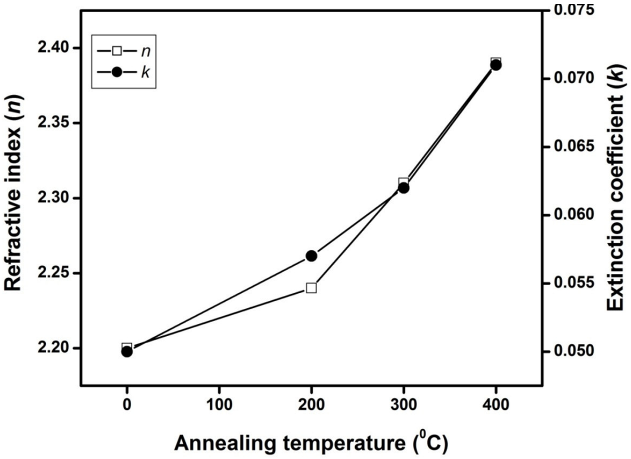

Figure 7. Refractive index and extinction coefficient of various annealing temperatures for CdSSe thin films.

We have further investigated the experimental data of optical reflectance and transmittance for CdSSe thin film to calculate the refractive index. Optical reflectance spectra were recorded at room temperature in air to obtain information on the optical properties of CdSSe thin films. Refractive index (n) of CdSSe thin films are estimate using the expressions [18-19],

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - k^2} \tag{6}$$

The variation of refractive index with wave length of incident radiation for CdSSe thin films is shown in Figure 7. Refractive index found to decrease as a function of wave length in CdSSe thin film prepared at optimized deposition condition. The extinction coefficient can be calculated by using the relation [20].

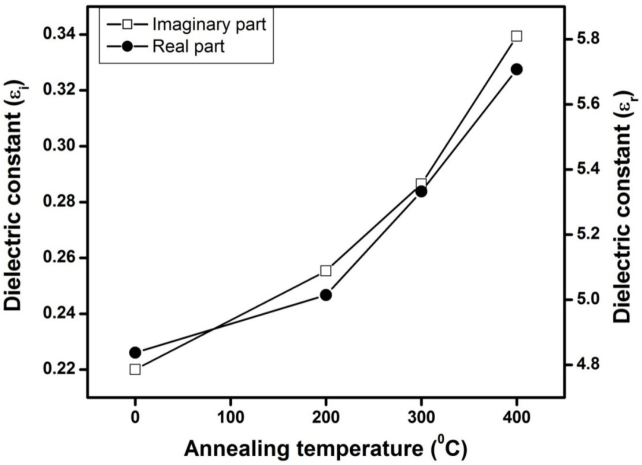

Figure 8. Real and imaginary part of dielectric constants with various annealing temperatures for CdSSe thin films.

$$k = \frac{\alpha\lambda}{4\pi} \tag{7}$$

where α is absorption coefficient, λ is wave length of the CdSSe thin films. The refractive index and extinction coefficient of the thin films are estimated from following equations (10) and (11). Figure 7 shows the refractive index, n, and the extinction coefficient, k, respectively, for electrodeposited CdSSe 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 [21]. The refractive index tends to decrease for both films as we approach longer wavelength regime. The refractive index was found to constant value after visible region. The refractive index and extinction coefficient of the films are increased when increasing the annealing temperature shown in fig. 7. The refractive index of the films increased rapidly with the increase of annealing temperature also extinction coefficient values. The initial sharp increase of ‘n’ with ‘k’ indicated a rapid change in the absorption energy of the unannealed films.

The complex dielectric constant is known to be a fundamental intrinsic material property. The real part of dielectric constant is associated with the property of slowing down the speed of light in the material. The real and imaginary parts (Figure 8) of the dielectric constant were determined using the relation [22]

$$\varepsilon = \varepsilon_r + \varepsilon_i = (n+ik)^2 \tag{8}$$

where ‘ε_r’ and ‘ε_i’ are the real and imaginary parts of the dielectric constant respectively and are given by

$$\varepsilon_r = n^2 - k^2 \tag{9}$$

and

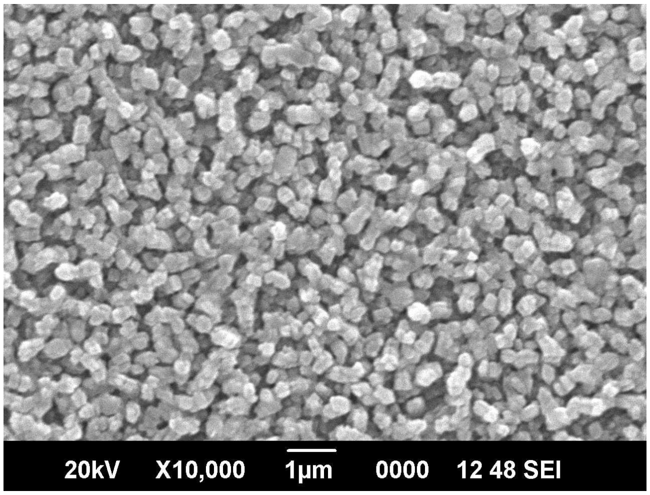

Figure 9. SEM picture of CdSSe thin film annealed at 400°C.

$$\varepsilon_i = 2nk \tag{10}$$

The imaginary part of the dielectric constant resembles the variation similar to extinction coefficient values and the variation is plotted simultaneously. The trend showed is typical of a semiconductor. The knowledge of the real and imaginary parts of the dielectric constant provides information about the electronic band structure; details of it are found [23]. ε_r and ε_i are found to vary with the increase in photon energy. This is based on stoichiometry of samples and the formation energy of defect levels. This is because the band gap increases with the deposition potential.

The surface morphology of 400^0 Cannealed CdSSe thin films was examined by scanning electron microsopy (SEM). Figure 9 shows the SEM picture of CdSSe electrodeposited annealed at 400^0C. At annealed (400^0C) films there is an increase in crystallite size. This result in an increase in nucleation over-growth and the deposits are more compact with uniform grain structure. An increase in the size of the crystallites with anneal temperature was also evident from the SEM picture. It is observed from scanning electron micrographs that the average grain sizes of CdSSe films annealed at 400^0C is 100nm. The grains become distinct larger by connecting to neighbors and appear as a number of stacking flakes in sizes up to more than 100 nm as shown in figure.

4. CONCLUSIONS

The optical and structural characterization on both un-annealed and annealed samples have shown that the thermal treatment carried out at 200^0C, 300^0 C and 400^0C has a great influence on the physical parameters of the grown structures. The XRD results reveal that the deposited thin film has a good polycrystalline hexagonal structure. On the films without annealing films has the crystallite size are lower than those films annealed temperature of 200^0C, 300^0C and 400^0C. The microstructural parameters were estimated and were found to depend on the post heat treatment the CdSSe thin films. It has been observed that the direct band gap energy was increased from 1.81 to 1.89 eV after annealing from 0 to 400^0C for

60 min under air medium. We propose that this increase in band gap energy may be due to the decrease cadimium compositiion after thermal treatment. The refractive index and extinction coefficient showed some variation with rise in annealing temperature of CdSSe film. An increase in the size of the crystallites with anneal temperature was also evident from the SEM picture. The annealing effects on the structural and optical properties of CdSSe thin film on conducting glass substrate will be useful for the formation of CdSSe based polycrystalline films for the application of optoelectric devices.

REFERENCES

[1] C.D. Lokhande, Mater. Chem. and Phys., 27, 1 (1991) .

[2] C.D. Lokhande, S.H. Pawar, "Proc. of Workshop on Solid State Energy Conversion", Kolhapur, India, May 1985.

[3] G. Hodes, J. Manssen, D. Cahen, in "Inorganic Synthesis", Ed., S.L. Holt, Wiley, New York, USA, 1983, p. 80.

[4] D.Raja Reddy, B.K. Reddy, "Proc. of Conference on the Physics and Technology of Semiconductor Devices and Integrated Circuits", Madras, India, Feb. 5-7, 1992.

[5] D. Bhattacharya, S. Mohanty, S.N. Sahu, "Proc. of Solid State Physics Symposium", Bombay, India, December 27-31, 1993.

[6] M.C. Tamargo, "Proceedings of the 2nd International Symposium on Blue Laser & Light Emitting Diodes", Chiba, India, 1998.

[7] A. Jia, J. Crystal Growth, 214/215, 1085 (2000).

[8] I.V. Bradley, J.P. Creasey, K.P. O'Donnell, J. Crystal Growth, 184, 728 (1998).

[9] R.S. Mane, C.D. Lokhande, Thin Solid Films, 304, 56 (1997).

[10]Guojia J. Fang, Dejie Li and Bao-Lun Yao, Thin Solid Films, 418, 156 (2002)

[11]Jianhua Hu, Roy G. Gordon, "AIP Conf. Proc.", 268, 381 (1992).

[12]B.D. Cullity, "Elements of X-ray Diffraction", Addison-Wesley Publishing Company Inc., UK, 1978.

[13]Gopal, S., C. Viswanathan, B. Karunagaran, Sa. K. Narayandass, D. Mangalaraj, J. Yi, Cryst. Res. Technol., 40, 557 (2005).

[14]S. Kose, F. Atay, V. Bilgin, I Akyuz, J. Mat. Chem. and Phys., 111, 351 (2008).

[15]T. Mahalingam, S. Thanikaikarasan, V. Dhanasekaran, A. Kathalingam, S. Velumani, Jin-Koo Rhee, Materials Science and Engineering B (Article in Press).

[16]M.H. Mamat, S. Amizam, H.A. Rafaie, H. Hashim, A. Zain Ahmed, S. Abdullah, M. Rusop , "AIP Conf. Proc.", 1017, 139 (2008).

[17]N. Bouhssira, S. Abed, E. Tomasella, J. Cellier, A. Mosbah, M. S. Aida, M. Jacquet, Appl. Surf. Sci., 252, 5594 (2006).

[18]N. Benramdane, W.A. Murad, R.H. Misho, M. Ziane, Z. Kebbab, J. Mat. Chem. and Phys., 48, 119 (1997).

[20]E. Fatas, P. Herrasti, F. Arjona, E. Garciacamarero and J.A. Medina, Electrochim. Acta., 32, 139 (1987).

[21]T. Mahalingam, V. Dhanasekaran, G. Ravi, Soonil Lee, J.P. Chu, Han-Jo Lim, J. Optoelectron. Adv. mater., 12, 1327 (2010).

[22]E. Marquez, J. Ramirez, P. Villares, R. Jimenez, P.J.S. Ewen, A.E. Owen, J. Phys. D: Appl. Phys., 25, 535 (1992).

[23]S. Thanikaikarasan, T. Mahalingam, M. Raja, Taekyu Kim, Y.D. Kim, J. Mater. Sci. Mater. Electron., 20, 727 (2009).