

STRUCTURAL AND OPTICAL CHARACTERIZATION OF VACUUM EVAPORATED ZINC SELENIDE THIN FILMS

Andalipa Islam

University of Dhaka, Dhaka, Bangladesh

Chitra Das

BRAC University, Dhaka, Bangladesh

Shamima Choudhury, Prof.

Mehnaz Sharmin

University of Dhaka, Dhaka, Bangladesh

Tahmina Begum

Atomic Energy Centre, Dhaka, Bangladesh

Abstract

Optical and structural characterization of Zinc Selenide (ZnSe) thin films (thickness ranging between 200 - 500 nm) prepared by vacuum ($\sim 10^{-6}$ Torr) evaporation method were investigated. The thin films were deposited with varying substrate temperature in the range 373 - 573K. Optical measurements were carried out with UV-VIS-NIR spectrophotometer with photon wavelength ranging between 300-2500 nm. The absorption coefficient, energy band gap, refractive index and extinction coefficient were determined using transmission and reflection spectra at the same wavelength range. The dependence of absorption coefficient in the photon energy had been determined. Analysis showed that direct transition occurred with band gap energies ranges from 2.6 eV to 2.9 eV. Refractive indices and extinction coefficients were evaluated in the above spectral range. For structural properties, 300nm films were deposited with varying substrate temperatures and were vacuum annealed in situ at 373 K for one hour. The X-ray diffraction (XRD) patterns showed polycrystalline nature of films having cubic (Zinc blende) structure. The most preferential orientation is along [111] direction for all deposited films together with other abundant planes [220] and [311]. Structural parameters such as lattice constant, grain size, internal stress, microstrain, dislocation density were calculated. The value of lattice constant was estimated to be 5.660 Å to 5.761 Å. The grain sizes were calculated to be which ranges between 266 Å to 384 Å. With the increase of substrate temperature the average grain size of the ZnSe films increases, as

revealed from the XRD studies.

Keywords: ZnSe thin films, Thermal evaporation, Optical Properties, Structural Properties

Introduction

Among many other inorganic materials, Zinc Selenide (ZnSe) has attracted considerable interest over the years owing to their wide range of applications in the field of optoelectronics. ZnSe is a II-VI compound semiconductor, where Zn is a divalent element and Se is a hexavalent element. This compound can be obtained as single crystals belonging to Zinc blende lattice with the lattice constant is 5.657\AA and energy gap is 2.7 eV at room temperature (Kissinger *et.al.*, 2009). ZnSe thin films are widely used in fabrication of various optoelectronic devices such as solar cells, blue-green light emitting diodes (LED's), blue laser diodes, laser screens, photo diodes, thin film transistors, photo electrochemical cells, dielectric mirrors etc (Antohe *et.al.*, 2013). There are various techniques often used for deposition of ZnSe thin films such as chemical bath deposition (CBD) technique (Okereke *et.al.*, 2011), Quasi-closed volume technique (Popa *et.al.*, 2011), sputtering (Rizzo *et.al.*, 2000), Hot wall evaporation technique (Pal *et.al.*, 1995), vacuum evaporation technique (Chu *et.al.*, 1992 and Das *et.al.*, 2013) etc. Thermal evaporation (Chaliha *et.al.*, 2008) is one type of vacuum evaporation technique which is a good method for preparation of thin solid films for scientific studies and many technological applications.

ZnSe thin films of constant thickness (300 nm) were deposited by thermal evaporation method in a different substrate temperature range (from room temperature to 200 °C) under a vacuum of 10^{-6} mbar (Bhuiyan *et.al.*, 2012) and the XRD pattern and optical parameters (transmittance, reflectance, absorption coefficient, band gap energy and refractive index) of the ZnSe films varied slightly from our annealed ZnSe films. Thermally evaporated ZnSe thin films of different thicknesses (200 nm – 450 nm) were deposited at various substrate temperatures (from room temperature to 523 K) under a vacuum of 10^{-5} Torr (Chaliha *et.al.*, 2008) and the XRD pattern obtained by the authors was similar to those obtained by us. ZnSe thin films of different thicknesses (500Å- 5000Å) were deposited onto glass substrate (Khairnar *et.al.*, 2012) by thermal evaporation technique at 373 K and under the vacuum of 10^{-5} Torr, transmittance and reflectance measurements in the spectral range 200 - 2500 nm revealed that the direct band gap increases with the increase of film thickness which is similar to our findings.

In present work, ZnSe thin films were deposited onto glass substrate at different thicknesses (200 nm – 500 nm) and at different substrate temperatures (373 K- 523 K) by thermal evaporation technique under a high

vacuum of 10^{-6} Torr. Optical measurements of the films were carried on to investigate the effect of substrate temperature and thickness on the various optical properties (transmittance, reflectance, absorption co-efficient, extinction co-efficient, refractive index and optical band gap) in the photon wavelength range 300nm-2500nm. ZnSe films of 300 nm thickness prepared at substrate temperatures 373 K, 473 K and 523 K were annealed at the temperature 373 K for 60 minutes to study the structural properties (lattice constant, grain size, internal stress, microstrain and dislocation density) of the films by X-ray diffraction method. Similar study of structural and optical properties were performed on undoped and Iodine doped Tin Oxide (SnO_2) thin films (Chowdhury *et.al.*, 2011) and Cadmium doped ZnS ($\text{Zn}_x\text{Cd}_{1-x}\text{S}$) thin films (Biswas *et.al.*, 2007) by the authors. The aim of our present work was to optimize the growth condition of ZnSe thin films to be useful in fabrication of optoelectronic devices.

Experimental

Thin films of ZnSe were deposited on to chemically and ultrasonically cleaned glass substrate by thermal evaporation in vacuum ($\sim 10^{-6}$ Torr) using an oil diffusion evaporation unit (Edwards, E306, UK), there were two pressure gauges, Pirani Gauge (measures low vacuum up to 10^{-3} Torr) and a very sensitive Penning Ionization Gauge (measures relatively high vacuum, from 10^{-2} Torr to about 10^{-8} Torr) to measure high vacuum. The source material ZnSe was in powdered form and it was evaporated from a molybdenum boat and the substrate was placed at a distance of 8 cm above the source. The films of thicknesses 300 nm were deposited at various substrate temperatures in the range 373 K- 523 K. The thickness and the rate of deposition of the films were measured in situ by a quartz crystal thickness monitor (FTM5, Edwards, UK). A radiant heater and a half-circle metallic substrate holder were used for heating the substrate.

Optical transmission and reflection coefficients of the ZnSe films were observed with the variation of wavelength of light within the range 300 nm - 2500 nm using a dual beam UV-VIS-NIR recording spectrophotometer (Shimadzu, UV-3100). Light source of the units was 50 W Tungsten-Halogen lamp and Deuterium lamp and there was a grating type monochromator. Signals coming from the samples were detected by an integrating sphere. A PHILIPS PW 3040 X' Pert PRO XRD system with angular range $20^\circ \leq 2\theta \leq 80^\circ$ was used to get X-ray data for the samples. Powder diffraction technique was used with a primary beam power of 40 KV and 30mA for Cu-K_α radiation, the recorded data were analyzed using computer software "X PERT HIGHSCORE".

Results and Discussion

Microstructural properties of the ZnSe thin films of thickness 300 nm grown at different substrate temperatures (373 K – 523 K) were studied from the X-ray diffraction (XRD) pattern which initially showed amorphous nature. The films were annealed at the temperature 373 K for 60 minutes. The XRD pattern observed for the annealed ZnSe films (Fig.1) indicate a preferential orientation along [111] direction which is the close packing direction of Zinc blende structure. In case of the films grown at the substrate temperature 523 K, the (111) diffraction plane is localized approximately at $2\theta=27.1^\circ$ and the other two weak peaks are approximately at $2\theta=45.5^\circ$ and 53.1° which match with the (220) and (311) diffraction plane of cubic phase ZnSe films and in good agreement with the XRD pattern reported by several authors (Mahalingam *et.al.*, 2007 and Murali *et.al.*, 2009). From these results it can be concluded that the elevated substrate temperatures are the suitable growth conditions to prepare good quality polycrystalline thin film. No other peak beside these is observed which establishes the single phase cubic structure of the films (Kalita *et.al.*,2000).

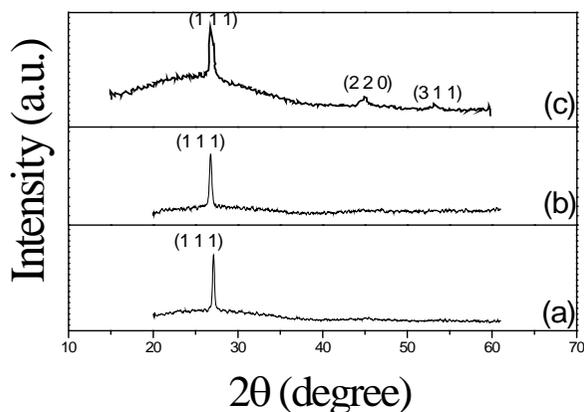


Figure 1. X-ray diffraction pattern of annealed ZnSe thin films grown at the substrate temperatures (a) 373 K, (b) 473 K and (c) 523 K

Lattice constant of all ZnSe thin films prepared at different substrate temperatures onto glass substrate for the cubic structure were determined from the following relation,

$$a=d\sqrt{(h^2+k^2+l^2)} \quad (1)$$

Where, (h k l) are the Miller Indices of plane.

Grain size of the deposited films was estimated using Scherrer formula (Warren, 1969),

$$D=k\lambda/\beta_{2\theta}\cos\theta \quad (2)$$

Here k was taken as 0.94, λ the wavelength of X-ray used and $\beta_{2\theta}$ the full width at half maximum of [111] peak of XRD pattern. Average internal stress developed in the films is determined by the relation (Chopra, 1979),

$$S = (E/2\gamma)(a_0 - a) / a_0 \tag{3}$$

Here E and γ are the Young's modulus and Poisson's ratio of ZnSe film. Standard bulk values of E and γ are used (Hearman, 1969) in calculation of stress a_0 is the bulk lattice constant perpendicular to the film plane.

Microstrain (ϵ) developed in the ZnSe film is calculated from the relation

$$\epsilon = (\beta_{2\theta} \cos \theta) / 4 \tag{4}$$

Where, $\beta_{2\theta}$ is the full width half maximum of [111] peak (Kalita *et.al.*, 2000).

The dislocation density is estimated from Williamson and Smallman method using the relation for cubic ZnSe thin films (Kalita *et.al.*, 2000),

$$\rho = 15\epsilon / aD \tag{5}$$

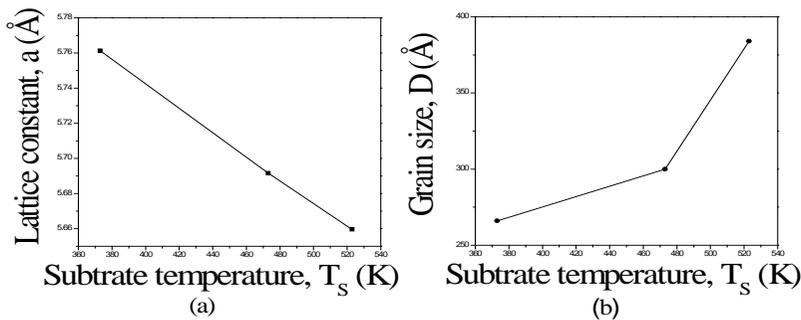


Figure 2. Variation of (a) lattice constant and (b) grain size with substrate temperature for annealed ZnSe thin films

Plot of lattice constant (Fig. 2a) against substrate temperature for the annealed ZnSe films shows a decreasing tendency with substrate temperature (Bhuiyan *et.al.*, 2012). The change in lattice constant for the deposited thin film over the bulk material clearly suggests that the film grains are strained and that may be owing to change of nature and concentration of the native imperfection. Density of the films is therefore expected to change in accordance with change of lattice constant (Reichelt *et.al.*, 1990). It is evident from Fig.2b that the grain size of vacuum evaporated ZnSe thin films are small and within the range 266 Å – 384 Å (Kissinger *et.al.*, 2009). The figure shows that grain size increases as the substrate temperature increases from 373 K to 473 K (Kalita *et.al.*, 2000).

The average internal stress is mostly compressional in nature as it shows negative value in Fig. 3. The compressional stress is also likely due to native defects arising from the lattice misfit. Compressional stress decreases with increase of T_s . At higher Substrate temperature (523K) it changes to tensile stress which indicates the predominant recrystallization process in the polycrystalline films (Kalita *et.al.*, 2000).

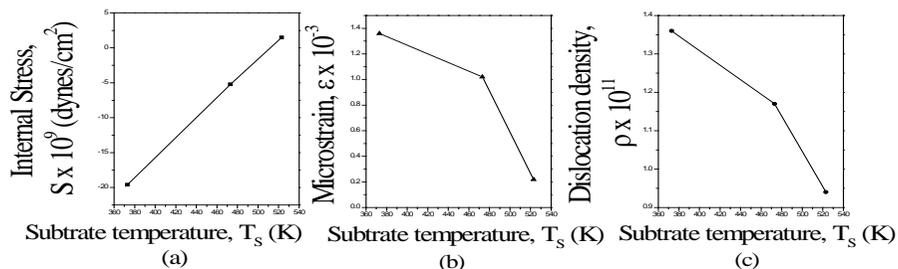


Figure 3. Variation of (a) internal stress, (b) microstrain and (c) dislocation density with substrate temperature for annealed ZnSe thin films

The average internal stress is mostly compressional in nature as it shows negative value in Fig. 3. The compressional stress is also likely due to native defects arising from the lattice misfit. Compressional stress decreases with increase of T_s . At higher Substrate temperature (523K) it changes to tensile stress which indicates the predominant recrystallization process in the polycrystalline films (Kalita *et.al.*, 2000).

From the Fig.3b and 3c, it is observed that both microstrain and dislocation density exhibit decreasing trend with substrate temperature. The decrease of microstrain and dislocation density at higher substrate temperature may be due to the movement of interstitial Zn atoms from inside the crystallites to its grain boundary which dissipate leading to reduction in the concentration of lattice imperfection. The decrease in the dislocation density and strain indicates the formation of higher quality films at higher substrate temperature (Chaliha *et.al.*,2008).

Optical transmittance and reflectance of ZnSe thin films prepared at various thickness (200nm – 500nm) and at various substrate temperatures (373 K- 523 K) were determined by UV-VIS-NIR spectroscopy in the photon wavelength range 300 nm- 2500nm. Transmittance and reflectance spectra of ZnSe thin films are illustrated in Fig.4.

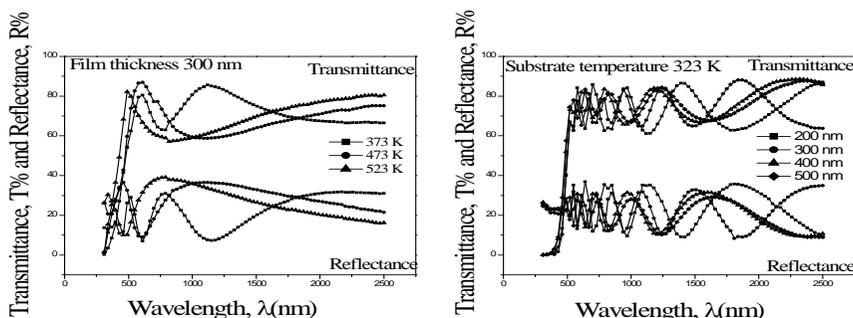


Figure 4. Transmittance and reflectance spectra in the wavelength range 300nm- 2500nm for ZnSe thin films

From Fig.4 it is seen that transmittance increases smoothly from a very low value to a maximum value in the visible region of wavelength and becomes almost consistent in the longer wavelength region. Sharp fall in transmittance in the ultraviolet-visible region of spectrum (at the band edge) indicates good crystallinity of the ZnSe films (Antohe *et.al.*,2013). The shift of transmittance peak toward the shorter wavelength region (higher energies) with the increase of substrate temperature is due to the structural improvement (Balkanaski *et.al.*, 2000). The films deposited at higher substrate temperature show higher transmittance in the visible region indicating better crystalline structure. The rise and fall in transmittance and reflectance is observed by other workers (Miah *et.al.*, 2010). Interference pattern with rise and fall is observed in the reflectance spectra of the films and it decreases in the near infrared region of spectra. The overall reflectance of the film decreases with the increase in the film thickness but it increases with the increase in substrate temperature which is related to the overall increase and decrease in absorbance.

Optical absorption is described quantitatively through the absorption co-efficient which gives a quantitative measure of band structure. It can be calculated from the transmittance and reflectance data. In an absorbing material absorption co-efficient is related to the refractive index of the medium and the wavelength of the incident light. Refractive index n is expressed as,

$$n = n_r - ik \tag{6}$$

Where n_r is the real part of refractive index and k is the extinction co-efficient. Extinction co-efficient k of a material at a wavelength can be related to its absorption coefficient by (Dutta *et.al.*, 2009)

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

Refractive index is calculated by the relation (3), Where, R is the optical reflectance.

$$n = \left(\frac{1+R}{1-R} \right) + \sqrt{\left(\frac{4R}{(1-R)^2} - k^2 \right)} \quad (8)$$

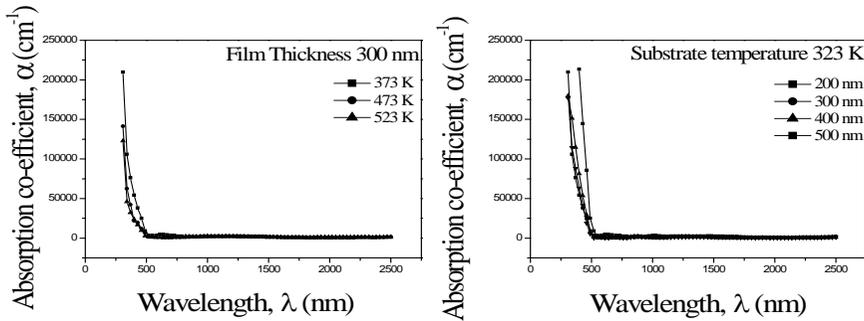


Figure 5. Variation of absorption co-efficient with wavelength (300 nm-2500 nm) for ZnSe thin films

It is observed from Fig. 5 that absorption co-efficient (α) increases with photon wavelength in the UV region of spectrum. Absorption co-efficient of the films decreases with the decrease of substrate temperature. It is obtained that absorption co-efficient variation is the highest in case of substrate temperature 373 K. This may be due to the presence of thermal lattice vibrations and imperfections. When the substrate temperature increases, it produces a significant shift in the energy absorption edge to the longer wavelength, which must be attributed to the growth of crystal grains (Bhuiyan *et.al.*, 2012). The decrease of absorption coefficient with the increase of film thickness indicates that the thicker films contain more atoms and reasonably more states available for the photons to be absorbed (Miah *et.al.*, 2010).

The nature of transition (direct or indirect) is determined by using the following relation (Patel *et.al.*, 1987), where $h\nu$ is the photon energy, E_g is the band gap energy, A and n are constants. For direct transition $n=1/2$ and indirect transition $n=2$.

$$\alpha = \frac{A(h\nu - E_g)^2}{h\nu} \tag{9}$$

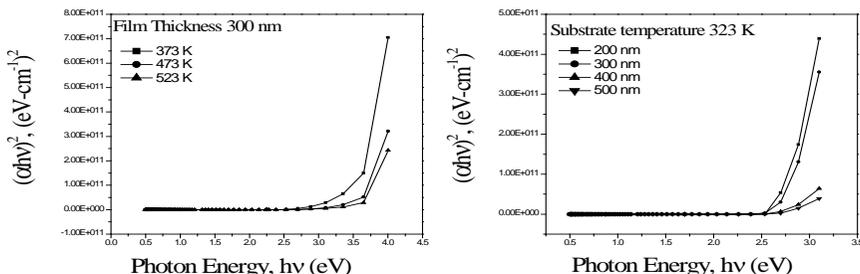


Figure 6. $(\alpha h\nu)^2$ versus photon energy graph for ZnSe thin films

Fig.6 shows that the variation of $(\alpha h\nu)^2$ with photon energy for the ZnSe thin films is linear at the absorption edge, confirming the direct band gap transition of ZnSe. Band gap (E_g) was determined by extrapolating the straight portion to the energy axis at $x=0$. The band gap energy calculated for the films grown at substrate temperature 373 K, 473 K and 523 K are 2.88eV, 2.94eV and 2.98eV respectively (Subbaiah *et.al.*, 2005). The E_g value for ZnSe film deposited at 373 K is 2.88 eV, which is ‘blue shifted’ by 0.18eV from the standard bulk E_g value of 2.70 eV (Kissinger *et.al.*, 2009). Optical band gap energy increases with the increase of substrate temperature which indicates the decreases in disorder and defects in the structural bonding. This can be explained by assuming that during the annealing process the films get enough time for some atomic rearrangement to take place and hence some defects get removed. It may be related with the variations in size and morphology of grains (Shadia, 2012). The band gap energy calculated for the films of thicknesses 200nm, 300nm, 400nm and 500nm grown at constant substrate temperature 323 K are 2.73eV, 2.75eV, 2.76 eV and 2.8 eV respectively. Optical band gap energy increases with the increase of film thickness which may be because of the formation of small grain size in the film (Khairnar *et.al.*, 2012).

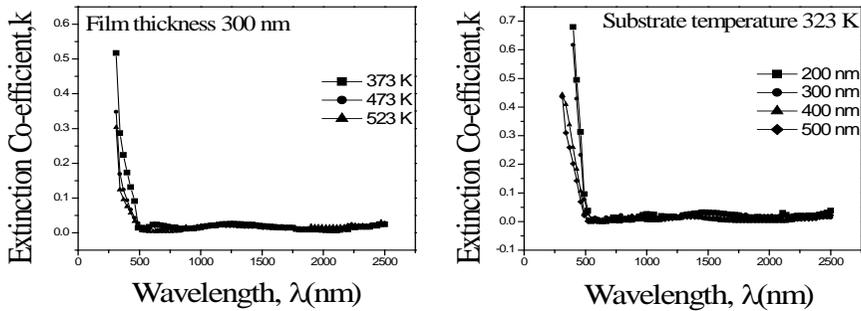


Figure 7. Variation of extinction co-efficient with wavelength (300 nm-2500 nm) for ZnSe thin films

Extinction co-efficient exhibits very high value near UV region indicating high absorption in that wavelength region and begins to decrease as the wavelength increases and seem to be saturated in the visible and infrared region (Okereke *et.al.*, 2011) which is nearly similar the behavior of absorption co-efficient for ZnSe thin film (Fig.7). It is also observed that the highest value of the extinction co-efficient decreases with the increase of substrate temperature which may be due to the variation of absorption of light at the grain boundaries which is almost consistent in the higher wavelength region. The increase of extinction coefficient with the photon energy indicates the probability of raising the electron transfers across the mobility gap with photon energy and greater attenuation of light in a thin film (Howari, 2012). The decrease of maximum value of extinction co-efficient with the increase of film thickness agrees with the behavior of absorption coefficient (Miah *et.al.*, 2010).

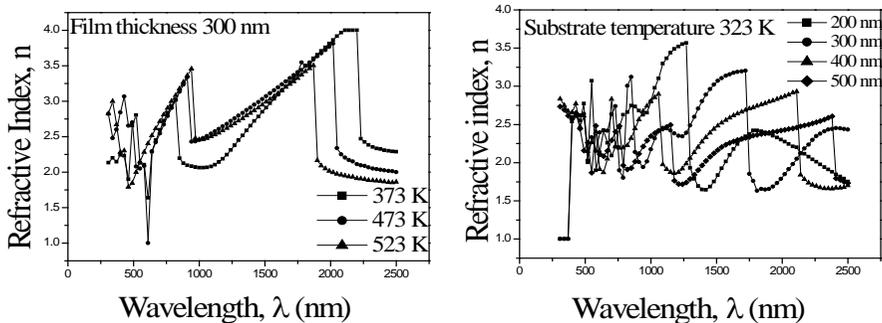


Figure 8. Variation of refractive index with wavelength in the range 300 nm-2500 nm for ZnSe thin films

Fig.8 shows a graph which is oscillatory in nature with some maxima and minima which increase with the increase of film thickness (Khairnar *et.al.*, 2012), but remains almost same with the increase of substrate temperature. Exponential decrease in the higher wavelength range is found here and also the positions of the shifts are changed. With the increase of substrate temperature the value of the peaks are also reduced. The shifting of curves to shorter wavelength may be due to the increase in the energy gap which causes the lattice to expand and the grain size to grow as a consequence to the decrease of defect states (Pal *et.al.*, 1995).

Conclusion

ZnSe thin films were deposited onto chemically and ultrasonically cleaned glass substrates at various thicknesses (200nm – 500nm) and at different substrate temperatures (323K -523K). The films showed high transmittance and reflectance in the visible region and high absorption in the UV region. Refractive index of ZnSe was oscillatory in nature within the wavelength range 300nm – 2500nm. Optical band gap value of the films increased with the increase of substrate temperature and film thickness and it was found in the range 2.6 eV - 2.9 eV. XRD pattern of the annealed ZnSe films showed polycrystalline fcc Zinc blende structure with a preferred orientation along the (1 1 1) plane. The crystalline quality increased with increasing substrate temperature which was understood by studying the microstructural properties. The average internal stress developed in the films deposited at higher substrate temperatures was tensile in nature. It can be concluded that ZnSe films grown at higher substrate temperature have nice optical and structural characteristics to be useful in fabrication of various optoelectronic devices.

Acknowledgement

Authors are thankful to Experimental Physics Division, Atomic Energy Centre, Dhaka providing necessary facilities.

References:

- Antohe S., Ion L., Girtan and Toma. Optical and morphological studies of thermally vacuum evaporated ZnSe thin films. Romanian Reports in Physics, 2013, Vol. 65, No. 3, pp. 805–811
- Balkanaski M. & Richard Fisher Wallis. Semiconductor Physics and Applications. Oxford University Press, Newyork, 2000
- Bhuiyan M.R.A. & Miah M.A.H. Begum. Substrate temperature effect on the structural and optical properties of ZnSe thin films. Journal of Bangladesh Academy of Sciences, 2012, Vol. 36, No. 2, pp. 233-240

- Biswas N.K., Choudhury S., Bhuyian and Hasan. Structural and Optical properties of vacuum evaporated $Zn_xCd_{1-x}S$ thin films. Journal of Bangladesh Academy of Sciences, 2007, Vol. 31, No. 2, pp. 205-212
- Chaliha S., Borah M.N., Sarmah and Rahman. Effect of substrate temperature on structural properties of thermally evaporated ZnSe thin films of different thickness. Journal of Physics Conference Series, 2008, Vol. 114, No. 1
- Chowdhury F. R., Choudhury S., Hasan and Begum. Optical properties of undoped and indium-doped tin oxide thin films. Journal of Bangladesh Academy of Sciences, 2011, Vol. 35, No. 1, pp. 99-111
- Chu T.L., Chu S.S. Chen, Britt, Ferekides and Wu. Zinc selenide films and heterojunctions. Journal of Applied Physics, 1992, Vol. 71, Issue 8, pp. 3865
- Das C., Begum J., (2013) Begum and Choudhury. Effect of thickness on the optical properties of GaAs thin films. Journal of Bangladesh Academy of Sciences, 2013, Vol. 37, No. 1, pp. 83-91
- Dutta S., Chattopdhyay, S. Sarkar, Chakrabarti, Sanya and Jana. Role of Defects in Tailoring Structural Electrical and Optical Properties of ZnO. Progress in Material Science, 2009, Vol. 54, Issue 1, pp. 89-136
- Hariskos D. & Spiering S. Powalla. Buffer Layers in Cu(InGa)Se₂ Solar Cells and Modules. Thin Solid Films, 2005, Vol. 480-481, pp. 99-109
- Hearman R. F. S., S. Balakrishna, M. Krishnamurthi and B. R. Rao. Physics of Solid State (eds). New York: Academic Press, 1969
- Howari H. Influence of pulsed laser annealing on the optical properties of thermally evaporated ZnSe thin films. Journal of Natural Sciences and Mathematics, 2012, Vol. 5, No. 2, pp. 139-154
- Kalita P.K.R. & Sharma B. K. Das. Structural characterization of vacuum evaporated films of ZnSe. Bull Matter Science, 2000, Vol. 23, No. 4, pp. 313-317
- Kasturi L. Chopra. Thin Film Phenomena. Malabar : Robert E. Krieger Publishing Co., 1979
- Khairnar U. & Behere S. Pawar. Optical properties of polycrystalline Zinc Selenide thin films. Materials Sciences and Applications, 2012, Vol. 3, pp. 36-40
- Kissinger N.J.S & Velmurugan N. Perumal. Substrate-temperature-dependent structural and optical properties of ZnSe thin films fabricated by using an electron beam evaporation technique. Journal of the Korean Physical Society, 2009, Vol, 55, No. 4, pp.1577-1581
- Mahalingam & Soonilee, Sunghvan and Yong. Studies of electrosynthesized ZnSe thin films. Journal of New Materials for Electrochemical System, 2007, Vol. 10, pp.15

- Miah M.A.H., Begum J. Uddin, Momin and Bhuiyan. Influence of thickness on the structural and optical properties of ZnSe thin films. *Journal of Applied Science and Technology*, 2010, Vol. 7, No. 2, pp. 27-32
- Murali K. R. & Xavier R. J. Characteristic of brush electroplated copper Selenide thin films. *Chalcogenide Letter*, 2009, Vol. 6, No. 12, pp. 683-687
- Okereke N.A. & Ekpunobi A. J. ZnSe buffer layer deposition for Solar cell application. *Journal of Non-Oxide Glasses*, 2011, Vol. 3, No. 1, pp. 31-36
- Pal R. & Maiti B. Choudhuri and Pal. ZnSe films: Preparation and properties. *Vacuum*, 1995, Vol. 46, Issue. 11, pp.1255-1260
- Patel S.M. & Kapale V.G. Optical properties of AgGaSe₂ thin films. *Thin Solid Films*, 1987, Vol. 148, Issue. 2, pp. 143-147
- Popa M.E. & Rusu G.I. Structural Characteristics and optical properties of ZnSe thin film. *Optoelectronics and Advanced Materials- Rapid Communications*, 2011, Vol. 5, No. 8, pp. 842-845
- Reichelt K. & Jiang X. The preparation of thin films by physical vapour deposition methods. *Thin solid films*, 1990, Vol. 191, Issue. 1, pp. 91-126
- Rizzo A. & Tagliente M.A., Caneve and Scalione. The influence of the momentum transfer on the structural and optical properties of ZnSe thin film prepared by r.f. magnetron sputtering. *Thin Solid Films*, 2000, Vol. 368, Issue. 1, pp. 8-14
- Shadia J. Ikhmayies. *Modern Aspects of Bulk Crystal and Thin Film Preparation*. Publisher: InTech, 2012
- Subbaiah Y. P. V. & Prathap P., Dekika and Ramakishna. Closed-Spaced evaporated ZnSe films: Preparation and characterization. *Physica B: Condensed Matter*, 2005, Vol. 365, 240-46
- Warren B.E. *X-ray Diffraction*. London: Addison-Wesley Publishing Co., 1969