JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. 6 No 4, 04007(4pp) (2014)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том 6 № 4, 04007(4cc) (2014)

Influence of Electron Irradiation on Optical Properties of ZnSe Thin Films

P. Raghu[1], C.S. Naveen[1], K. Mrudula[1], Sanjeev Ganesh[2], J. Shailaja[1], H.M. Mahesh[1,*]

[1] *Department of Electronic Science, Bangalore University, Jnanabharathi, Bangalore – 560056 Karnataka, India*
[2] *Microtron Centre, Mangalore University, Mangalagangothri, Mangalore – 574199 Karnataka, India*

(Received 05 July 2014; revised manuscript received 17 July 2014; published online 29 November 2014)

Zinc Selenide (ZnSe) thin films of 500 nm thickness were deposited by electron beam evaporation technique and irradiated with 8 MeV electron beam for the doses ranging from 0 Gy to 1 kGy. Optical properties were studied for both irradiated and pristine samples using Ultraviolet-Visible spectrophotometer. The increase in electron dose tends to decrease in transmittance and increase in refractive index of thin film. Irradiated thin film exhibits minimum of 67 % transmittance for 800 Gy with very high absorption of optical energy at 550 nm wavelength. The samples irradiated > 800 Gy tends to redeem the pristine properties. Optical band gap for irradiated thin film were direct and in the range of 2.66 – 2.69 eV.

Keywords: E – beam Evaporation, Optical properties, Electron radiation, Thin films, ZnSe.

PACS numbers: 61.80.Fe, 81.15.Jj, 78.30.Fs, 78.66. – w

1. INTRODUCTION

Zinc Selenide (ZnSe) is one of the most prominent candidate for photovoltaic device as an n-type buffer material in CdTe based solar cell due to its wide band gap of 2.67 eV [1]. ZnSe thin films have attracted several researchers for improving the efficiency of heterojunction solar cells. It has an immense potential to use as an efficient window/buffer material when CdS thickness is relatively small (< 100 nm) in CdS / CdTe solar cell. Also, it has wide transmission range from 450 nm to 21.5 μm with high refractive index of 2.60 at 550 nm and high electrical resistivity (10^{12} Ωcm) [2, 3]. ZnSe thin films are also used as buffer layers for CIGS solar cells which reached the efficiency up to 9.6 % (under AM 1.5 illumination) [4]. It has been reported that, by integrating different buffer layers in combination of zinc and tin oxide improved CdTe / CdS cell efficiency [5-7]. Several researchers has investigated, ZnSe as a buffer layer by exploiting the optical properties for replacement or along with reduced thickness of CdS [8-11]. Ionizing radiation produces the change in physical properties such as optical, structural, electrical, etc., Due to these factors, electron irradiation is included in thin film formulations. The functions of electron irradiation include softening films, reducing brittleness, increasing flexibility and ductility. Therefore, present investigation aims at examining the effects of electron irradiation on ZnSe thin films and possibility of using it as a buffer layer for solar cells.

2. EXPERIMENTAL

2.1 Preparation of Thin Films

The PVD apparatus used for deposition is based on a commercial system developed by Hind High Vac. Co., Bangalore. ZnSe powder source (99.99 % purity, Sigma Aldrich, U.S.A) is brought into the chamber in a molybdenum crucible in vacuum condition at a pressure of 2×10^{-5} mbar. Soda lime glass slides of dimensions 25 mm × 15 mm × 1.35 mm were used as substrate were degreased with soap water followed by ultrasonication in double distilled water and ethanol. The substrate holder is aided with continuous rotation for formation of uniform films on substrate surface. Thin films of 500 nm thickness were deposited at constant deposition rate of 5-8 A°/sec. Thickness and deposition rate were measured using quartz crystal thickness monitor (DTM-101).

2.2 Post Deposition Process

The aim of this post-deposition process (such as thermal annealing and electron irradiation) is commonly used to improve the structural, morphological and chemical quality of deposited thin films. Therefore, deposited samples were annealed in air ambient at 100° C for 3 hrs. After finishing thermal annealing treatment, samples were subjected to 8 MeV electron beam irradiation for doses ranging from 200-1 kGy in steps of 200 Gy, using variable energy Microtron accelerator facility available at Microtron Centre, Mangalore University, India. The dose delivered was measured with an alanine dosimeter close to the sample, and features of Microtron are detailed elsewhere [12, 13].

2.3 Characterization

Electron irradiated ZnSe thin films of different doses were characterized for optical parameters and were compared with unirradiated. Optical investigations of thin films were performed using VIS-NIR spectrophotometer (Ocean Optics, USA. Model No. USB4000-XR). Optical absorption is a useful method for investing the induced transition and providing information about band structure and optical energy gap of the materials. The principle of this technique is that, photons with energies higher than band-gap energy will be absorbed [14]. Absorption coefficient 'α' can be calculated using relation [15],

$$\alpha = \left[\frac{2.303}{d}\right] \times \log\left(\frac{1}{T}\right) \tag{1}$$

---

[*] hm_mahesh@rediffmail.com

It is also written as a function of incident photon energy ‘$h\nu$’ [16],

$$\alpha h\nu = A_0\left(h\nu - E_g\right)^P \tag{2}$$

Where, E_g is optical band gap, ‘P’ has discrete values like 1/2, 3/2, 2 or more depending on whether the transition is direct or indirect and allowed or forbidden. In the direct and allowed cases $P = 1/2$. Value of ‘P’ determines the nature of optical transition. The results have been analyzed according to the relation (2). A_0 is a constant and given by,

$$A_0 = \left[e^2 \Big/ \left(neh^2 m_e^*\right)\right](2m_r)^{3/2} \tag{3}$$

Where, m^*_e and $\underline{m_r}$ are effective and reduced masses of charges carriers respectively. The variations of extinction coefficient (k) with photon can be observed that wavelengths regardless of their thickness, values for extinction coefficients is calculated using the equation,

$$k = \frac{2.303\lambda \log\left(1/T_0\right)}{4\pi d} \tag{4}$$

3. RESULTS AND DISCUSSION

Figure 1 illustrates transmittance spectra of 500 nm ZnSe thin films – deposited and irradiated with different dose (200 Gy-1 kGy). At 550 nm, unirradiated ZnSe thin film exhibits high transmittance of 75 %, as the dose increased from 200 Gy to 1 kGy the transmittance has been decreased upto 800 Gy and at 1 kGy dose transmittance has been increased slightly (Fig. 2). This attributes to improvement in absorption after irradiation from 200 Gy to 800 Gy. The width of transmission edge shifted towards lower energy with increasing irradiation doses. Hence the influence of irradiation directly affects the absorption of thin film.

Figure 3 represents optical absorption spectra of ZnSe films deposited on glass substrate. Absorption coefficient was calculated from transmittance spectra for the film irradiated with different electron dose. The variation in absorption coefficient with wavelength reveals a very low absorption of energy in visible region and high absorption in shorter wavelengths. The spectra also confirm that, as the irradiated dose increases there is an increase in absorption at 550 nm. This attributes to the decreased transparency of thin film.

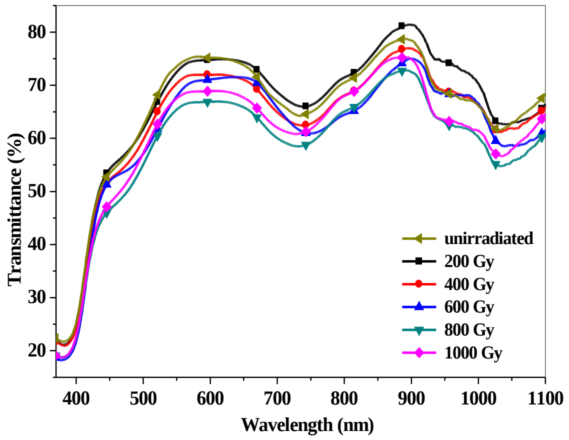

Fig. 1 – Transmittance spectra of irradiated ZnSe thin films of 500 nm thickness)

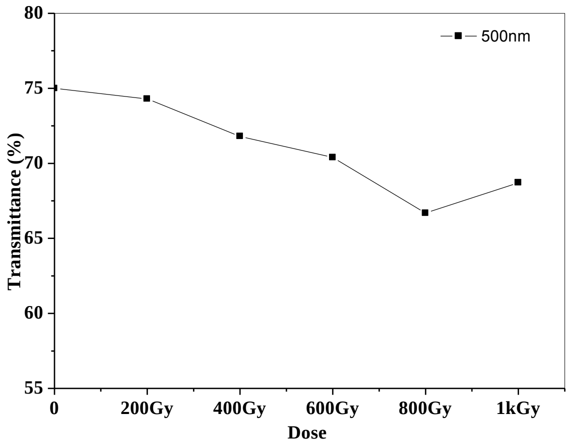

Fig. 2 – Transmission versus Dose of irradiated ZnSe Thin films

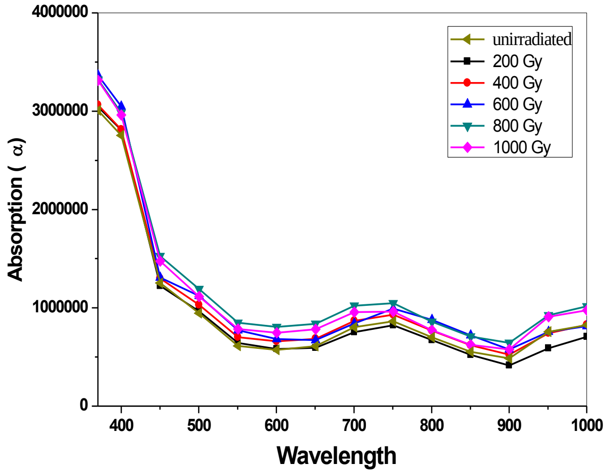

Fig. 3 – Absorption coefficient versus wavelength of ZnSe thin films

The direct band to band transition energies and tail width of pristine and irradiated film is represented in table 1. Pristine film has direct band gap of 2.68 eV which is equal to standard bulk band gap [17]. Optical band-gap value for de posited film for different dose varies in the range of 2.66-2.69 eV. This variation in optical band gap trend is because of increase in irradiation energy. The free atoms are responsible for creating several overlapping levels resulting in more energy inturn create multiple overlapping bands within thin films [18]. This phenomenon can be explained by Urbach tail which signifies characteristic phenomena of absorption curve with respect to photon energy (Fig. 4)

If structure of thin film has disorderness, we can estimate the level using Urbach energy [19] which results in lean-in transmittance spectra towards minimum photon energy. Tail width of thin films can be calculated by slope of straight line portion of plot (Fig. 4). The minimum tail width of 0.56 eV revealed by 600 Gy. Whereas, 1 KGy irradiated film exhibits higher tail width of 1.02 eV which is almost equal to pristine sample.

Table 1 – Variation of Band gap and tail width of irradiated ZnSe thin films

Sl. №.	Electron Dose (Gy):	Pristine	200	400	600	800	1000
1	Band Gap (eV):	2.68	2.69	2.68	2.69	2.66	2.67
2	Tail Width (eV):	1.03	0.87	0.85	0.56	0.90	1.02

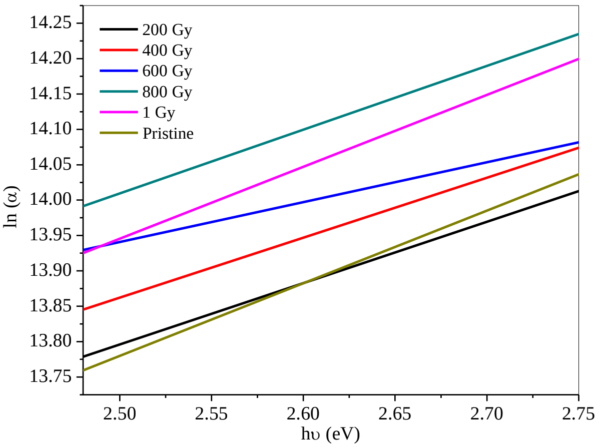

Fig. 4 – Variation of ln(α) versus photon energy of ZnSe thin films

This behavior highlights that higher dose can retain the properties of un-irradiated thin film. This is also evident from figure 3 that absorption has increased for lower dose and there after decreases, which inturn replicates better transmittance property.

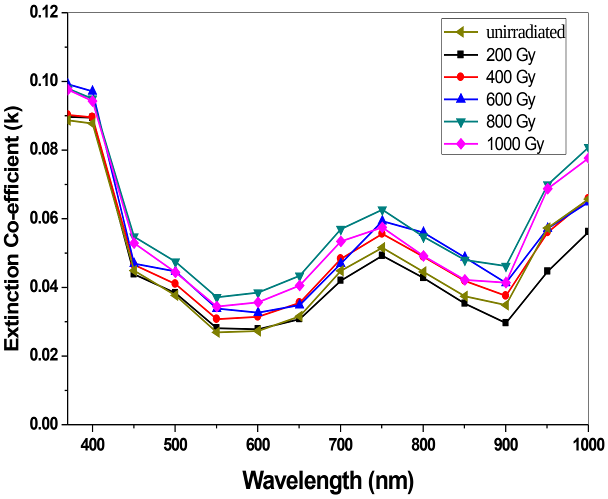

Fig. 5 – Variation of Extinction Coefficient vs wavelength of irradiated ZnSe Thin films

The extinction coefficient (k) is directly related to absorption of light. In the case of polycrystalline films, extra absorption of light occurs at grain boundaries [20]. This leads to non-zero value of 'k' for photon energies smaller than the fundamental absorption edge [21]. This is further confirmed by figure 5.

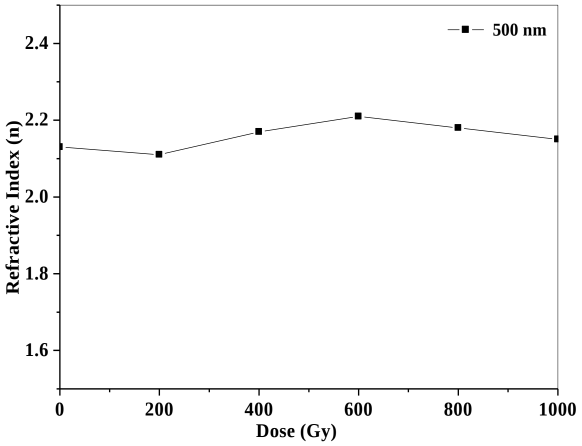

Fig. 6 – Variation of refractive index versus dose rate of 500 nm ZnSe thin films

The refractive index 'n' of the deposited films is evaluated from envelope technique is shown in figure 6. The maximum refractive index is found to be 2.21 for 600 Gy irradiated film. All values were found to be wavy nature, while higher energy dose will retain the value of pristine sample.

4. SUMMARY

Electron irradiation on 500 nm ZnSe thin films was found to induce changes in optical properties depending on irradiation dose: irradiation leads to decrease in transparency of thin film while higher dose of 1 KGy leads to decrease in absorption with increase in transparency equal to pristine sample. The film posses direct transition with optical band gap in the range of 2.66-2.69 eV and also exhibit maximum refractive index for 600 Gy and minimum for 1 KGy dose. The decrease in transmittance and refractive index after 800 Gy (i.e., for 1 KGy and above) has to be investigated.

AKNOWLEDGEMENTS

Authors would like to express their sincere thanks to BRNS-DAE, Govt. of India for the financial support vide major research project (Sanction No: 2011/34/19/BRNS/0080) under which this work has been carried out.

REFERENCES

1. W.S. Lour., C.C. Chang, *Solid-State Electron.* **39** No 9, 1295 (1996).
2. G. Grebe, G. Roussos, H. J. Schulz, *J. Phys. C* **9**, 4511 (1976).
3. G. Jones, J. Woods, *J. Phys. D* **9**, 799 (1976).
4. A. Rumberg, Ch. Sommerhalter, M. Toplak, A. Jager Waldau, Ch. M. Lux Steiner, *Thin Solid Films* **362**, 172 (2000).
5. X. Wu, P. Sheldon, *National center for photovoltaics reviews meeting,* report No NREL/CP-520-25656, 1 (1998).
6. G. Gordillo, *Photovoltaic specialist Conference – (Conference Record of the Twenty-Ninth IEEE:2002),* 644 (IEEE: 2002).
7. D.M. Sharafat Hussain, Nowshad Amin, *Chalc. Lett.* **8** No 3, 187 (2011).
8. P. Raghu, C.S. Naveen, J Shailaja, S. Ganesh, S.I. Murugaiya, H.M. Mahesh, *Int. J. Mat. Sci. App.* **3** No 3, 116 (2014).
9. O. Toma, R. Pascu, M. Dinescu, C. Besleaga, T.L. Mitran, N. Scarisoreanu, S. Antohe, *Chalc. Lett.* **8** No 9, 541 (2011).
10. S. Antohe, V. Ghenescu, S. Iftimie, A. Radu, O. Toma, L. Ion, *Dig. J. Nanomater. Bios.* **7** No 3, 941 (2012).
11. M. Ghenescu, L. Ion, I. Enculescu, C. Tazlaoanu, V.A. Antohe, M. Sima, M. Enculescu, E. Matei, R. Neumann, O. Ghenescu, V. Covlea, S. Antohe, *Physica E* **40** No 7, 2485 (2008).
12. K. Siddappa, Ganesh, S.S. Ramamurthy, H.C. Soni, P. Srivastava, Y. Sheth, Hemnani, *Radiat. Phys. Chem.* **51** No 4-6, 441 (1998).
13. Ganesh, K.C. Prashanth, Y.N. Nagesha, A.P. Gnana Prakash, D. Umakanth, M. Pattabi, K. Siddappa, S. Salkalachen, A. Roy, *Radiat. Phys. Chem.* **55** No 4, 461 (1999).
14. A.A. Abdel-Fattah, H.M. Abdel-Hamid, R.M. Radwan, *Nucl. Instr. Meth. B* **196**, 279 (2002).
15. S. Venkatachalam, S. Agilan, D. Mangalaraj, S. K. Narayandass, *Mater. Sci. Semicond. Process.* **10** No 2-3, 128 (2007).
16. J.J. Pankove, *Optical Processes in Semiconductors* (Prentice Hall:1971).
17. S. Venkatachalam, D. Mangalaraja, Sa.K. Narayandass, K. Kim, J. Yi, *Physica B* **358**, No1-4, 27 (2005).
18. N.A. Okereke, I.A. Ezenwa, A.J. Ekpunobi, *J. Non-Oxide Glasses* **3**, No 3, 105 (2011).
19. F. Urbach, *Phys. Rev.* **92**, 1324 (1953).
20. T. Mahalingam, M. Radhakrishnan, C. Balasubramaniam, *Thin Solid Films* **78**, No 3, 229 (1988).
21. H. Metin, R. Esen, *Semicond. Sci. Technol.* **18**, 647 (2003).