EFFECT OF THICKNESS ON THE OPTICALPROPERTIES OF ZINC SELENIDE THIN FILMS

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The zinc selenide (ZnSe) thin films of thicknesses 1.60µm and 1.64µm were chemically deposited on well cleaned glass substrate at room temperature. The films are polycrystalline with cubic structure, confirmed by x-ray diffractogram. The optical spectra of zinc selenide thin films were recorded in the wavelength range of 0.36µm and 1.10µm. The spectral absorption data shows that the films absorb in the ultra violet range of 0.36-0.45 microns and have almost zero absorbance in VIS-IR regions of the spectrum. The films have average index of refraction of 2.0. The plot of α^2 versus h□ showed a direct band gap range of 2.70eV-2.75eV. The band gap is found to decrease with increase in film thickness.

(Recieved October 19, 2011; accepted September 23, 2011)

Keyword: Semiconductor, thin film, Zinc selenide, chemical bath, characterization, application.

1. Introduction

The 11-VI semiconductor compounds are important optoelectronics, luminescent and laser materials. Intensive research has been performed in the past to study the fabrication and characterization of these compounds in the form of thin films. Zinc selenide is a widely used 11-VI semiconductor. It is one of the most interesting binary wide band gaps of about 2.7eV at room temperature. It has cubic/or hexagonal crystal structure. It is considered as an important technological material due to their potential applications in various optical and electronic devices and as window material for thin film hetero-junction solar cells (Scitz *et al,* 2002 and Hariskos *et al*,2005). The properties of interest in most of these applications are the energy band gap, film thickness and the wavelength of transmission or absorption of the films. Various methods have been employed for deposition of ZnSe thin films, which include thermal evaporation, electrochemical deposition and chemical bath deposition (Kale *et al*,2006 andOkereke and Ekpunobi 2011). The chemical bath deposition technique (Wang *et al,* 1999) has been found to be an inexpensive and simple low temperature method that could be used to produce good quality film for device applications. It is well studied and produces films that have comparable structural and opto-electronic properties to those produced using other sophisticated thin film deposition technique. This paper reports the chemical bath deposition of ZnSe thin films from an aqueous solution bath containing Zn $(NO_3)_2$ and $SeSO_3$, using EDTA as the complexing agent. X-ray diffraction which illustrates the formation of this material as well as its optical properties is presented.

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2. Material and methods

The preparation of ZnSe thin films on glass substrate is carried out using the chemical bath deposition (CBD) technique. The basic principle of the CBD technique consists the controlled generation of the metal and chalcogenide ions in an alkaline medium and their precipitation on the substrate in order to form a film. The deposition bath was prepared as follow: 10ml of 0.1M of EDTA was added to 10ml of 0.5M of Zn $(NO_3)_2$ in a 100ml beaker. To this was added 10ml of 0.1M of $SeSO_3$ and the volume was made up to 100ml with distilled water. The deposition was carried out at room temperature ~ 26°C for pH value of 10.2 and for different duration's 15-18hrs. At the end of each predetermined period of deposition, the coated substrates were taken out of the bath, washed well with distilled water and dried. The thickness of the film was measured using the optical method by Theye,(1985). The chemical reactions involved in the deposition of ZnSe thin films are as follow:

$$Zn(NO_3)_2 + EDTA \rightleftharpoons [Zn(EDTA)]^{2+} + 2NO_3^-$$

$$[Zn(EDTA)]^{2+} \rightleftharpoons Zn^{2+} + EDTA$$

$$SeSO_3 + OH^- \rightleftharpoons HSe^- + SO4^{2-}$$

$$HSe^- + OH^- \rightleftharpoons Se^{2-} + H_2O$$

$$Zn^{2+} + Se^{2-} \rightleftharpoons ZnSe \downarrow$$

Structural and optical characterization of the deposited films were carried out using an x-ray diffractometer with Cukα radiation and Janway 6405 UV-VIS model of spectrophotometerrespectively. From the spectrophotometer, the absorbance in arbitrary unit was measured. Parameters such as transmittance, band gap, refractive index and extinction coefficient were calculated.

3. Results and discussion

3.1 Structural analysis of znse films.

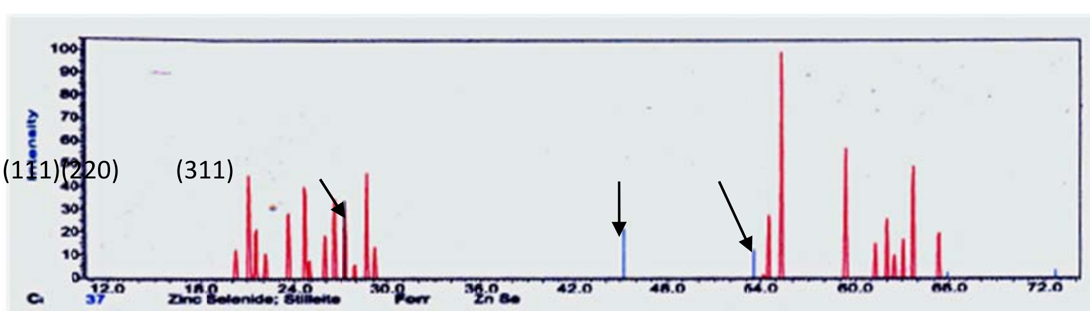

Fig. 1. X-ray diffraction spectra of ZnSe

Figure-1 shows the x-ray diffraction spectra of zinc selenide thin films prepared at room temperature (26°C). The figure reveals the existence of (111), (220) and (311) planes of reflections of cubic structure of ZnSe thin film. The lattice constant as was given in the XRD analysis and is found to be **a** =5.668Å. The results are in good agreement with the reported values by Mahalingam *et al*, (2007) who reported the XRD pattern of electro synthesized ZnSe film showing (111), (220), (3II) and (400) planes. Murali and Xavier(2009) obtained a film of orientations (111), (220) and (311) with the dominant orientations at (111) of pulsed electrodeposited ZnSe films. The results show that the greatest intensity is in (111) plane. This confirmed that the preferred orientation lies along the (111) plane which confirmed that the polycrystalline ZnSe were deposited in this work.

3.2 optical properties of ZnSe films:

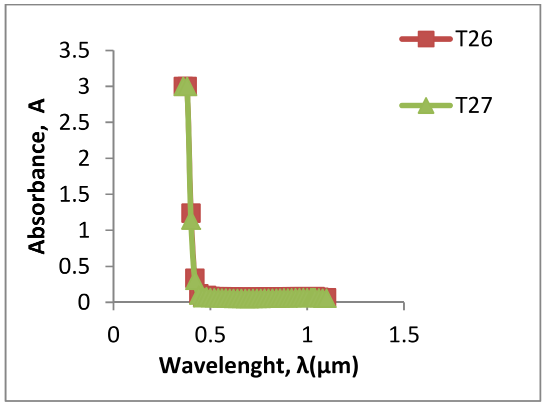

Fig. 2: Spectral absorbance of ZnSe films

The optical absorption spectra of ZnSe films deposited onto a glass substrate were studied at room temperature in the wavelength range of 0.360µm-1.10µm. The optical absorbance and transmittance spectra were obtained for the film deposited at different duration's 15-18hrs. The variation of optical absorbance with wavelength in figure-2 reveals a very low absorption of energy in the VIS-IR regions and sometimes close to zero and high absorptionin ultra violet region with a peak value of 3. This makes the film a good window layer for solar cell application. The low absorption of energy makes ZnSe useful for optical components in high laser window and multispectral applications, providing good imaging characteristics (Devyatykh *et al*, 1993). The optical absorbance decreases as the film thickness increases.

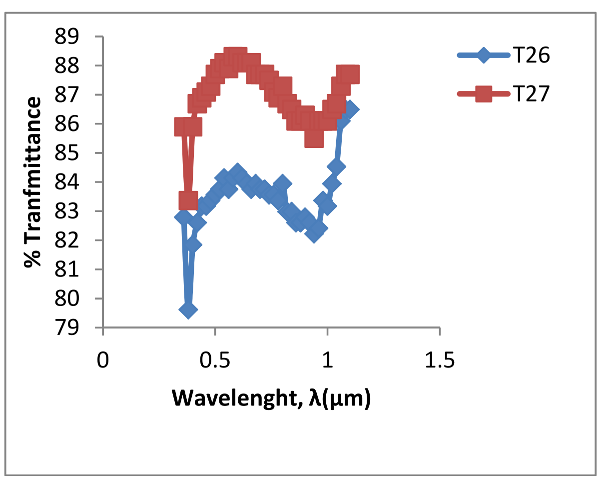

Fig. 3. Spectral transmittance of ZnSe

The transmittance spectra in figure -3 indicate a high transmission which is greater than 80% in VIS &IR regions of the spectrum. The higher transmittance in the visible regions makes it a strong candidate for use in optoelectronic devices. The spectra also reveal wide transmission range covering 0.4µm – 1.10µm. This makes the material useful in manufacturing optical components, windows, mirrors, and lenses for high power IR laser (Lokhande*et al*, 1998). The film thickness increases as the optical transmittance increases.

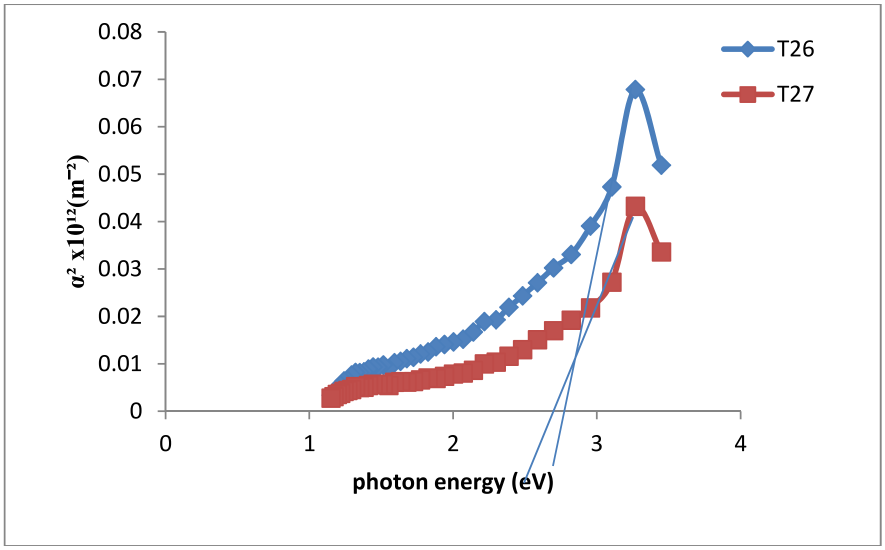

Fig. 4. Plot of α^{2}versus photon energyfor ZnSe

Figure- 4 shows the plot of α^2 versus h□ of ZnSe film. The linear dependence showed by α^2 with h□ indicates that the transition is direct. The band gaps were determined by extrapolating the straight portion to the energy axis at x = 0. The energy gaps were foundto be between 2.70eV - 2.75eV which were in good agreement with earlier reports by Murali and Xavier (2009)andMahalingam*et al*, (2007) who presented a band gap of 2.64 – 2.68 eV and 2.66 eV respectively. The wide band gap possessed by ZnSe film makes it likely candidate to replace material like GaN in light emitting laser diodes (Gutowski *et al*, 2002). Figure- 4 shows that the band gap decreases as the film thickness increases. The variation of film thickness with energy band gap of ZnSe film is shown in table-2.

Table-2:Variation of band gap with film thickness.

Reaction Bath	Film Thickness (µm)	Time of Deposition (hr)	Band gap (eV)
T_{26}	1.60	15	2.75
T_{27}	1.64	18	2.70

It is found thatthe band gap of zinc selenide is thickness dependent. The increase in film thickness results in decrease in energy band gap of ZnSe films. This is true because with increase in film thickness the individual levels of the free atoms will broaden the energy bands and create overlapping levels .This occurs when atoms are brought closer to each other. Hence with high film thickness there are several energy levels resulting in several overlapping energy bands in the band gap of these films. The overlapping energy bands therefore tend to reduce the energy band gap, Okujiagu (1992), Okujiagu and Okeke (2000a and b) resulting in lower band gaps for thicker films.

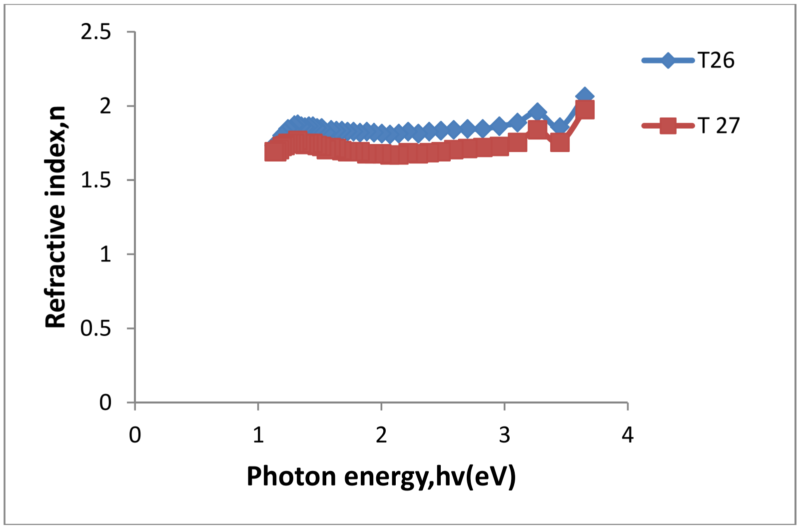

Fig. 5: Plot of refractive index versus photon energy of ZnSe

Figure-5 shows the plot of refractive index (n) as a function ofphoton energy. It decreases with increase in film thickness.The figure displays a high refractive index with a range of 2.0 – 2.4. These results are in close agreement with what was reported by Kale *et al,* (2006).The high refractive index possessed by ZnSe films made it suitable as anti-reflection.

The extinction coefficient (k) was estimated from

$$K = \frac{\alpha\lambda}{4\pi}$$

The range of values obtained for it is 4.2-10.2. Graphs of k as a function of photon energy are shown in figure-6. The extinction coefficient decreases as the thickness increases. This shows that the films have the least absorption in the VIS and IR regions but very high rate of absorption in the UV region. These optical properties makes ZnSe thin films nice glazing material for maintaining cool interior in buildings in warm climate regions while still keeping the rooms well illuminated. It is important to ensure that the thermal radiation from the warm glazing to the interior is inhibited. And enhanced convective heat transfer of the glazing to the exterior predominantly transfers the thermal energy dissipated in the glazing due to absorption to the exterior. It was, therefore, suggested in (Nair and Nair 1989) that reflectance in the spectral region should be strengthened while encouraging low thermal emittance.

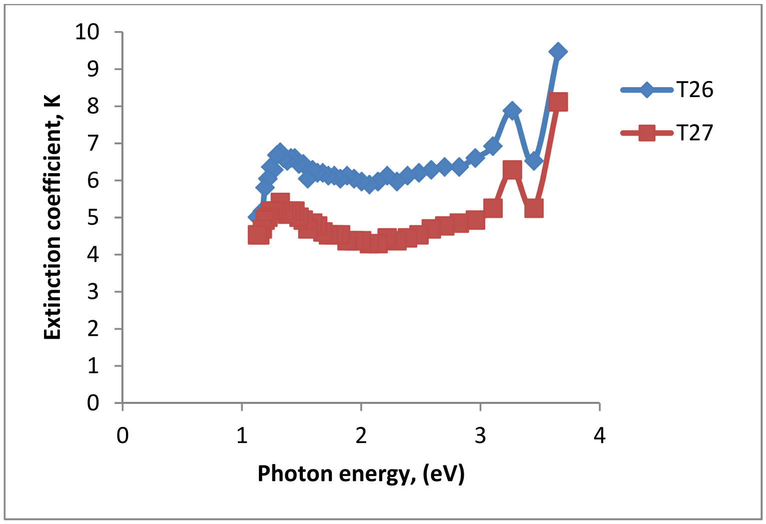

Fig. 6. Plot of extinction coefficient versusphoton energy of ZnSe

4. Conclusion

ZnSe films were successfully carried out using chemical bath deposition technique. Good quality films of Zinc selenide with cubic structurewere deposited. The preferred orientation of the crystallite lies along (111) planes. The films have peak transmittance in the visible region of the electromagnetic spectrum and high rate of absorption in the UV region. These make the films excellent glazing material for solar control in warm climate regions. The high transmittance makes the films potential for use in manufacturing optical components, windows, mirrors, and lenses for high power IR laser. The band gap was found to be direct and ranges from 2.65eV- 2.70eV.

References

[1] Devyatykh, G.G., Koshunov I.A., and Gavrishahuk E.M. Doklady A.N. USSR Russia **T28** 1, 56-57. ,(1993)
[2] Gutowski J. P., Michele H.I., Ruckmann H.G., Brunig M., Rowe K., Sebald and Voss TPhys. Stat. Sol. **B 234,** 70-83. .(2001).
[3] Hariskos D.S, Spiering and M. Powalla, Thin Solid Films. **480-481,** 99-109. (2005).
[4] Kale, R.B., S.D. Sartale, V. Ganessan, C.D. Lokhande, V.F. Lin, S.Y. Lu, Applied Surface Sci., **253**: 930-936. (2006).
[5] Lokande, C.D., P.S. Patit, A. Enniwi and H. Tributch, Applied Surface Sci., **123-124**,294 (1998).
[6] Mahalingam, T. A., Kathalingam I. S., Lee S. Moon and Y.D. Kim, J. New Mater. Electrochem. Syst., **10**,15-19 (2007).
[7] Murali, K.R. and R.J. Xavier, Characteristics of brush electroplated copper selenide thin films.Chalcogenide Lett., **6**: 683-687. (2009).
[8] Nair, M.T.S. and Nair,P.K. Semicond. Sci. Technol., **4,** 191-199 (1989).
[9] Okujiagu, C.U. and C.E. Okeke, Nig. J. Renewable Energy, **8**: 90-98 (2000a).
[10] Okujiagu, C.U. and C.E. Okeke, Nig. J. Renewable Energy, **8**: 24-23. (2000b).
[11] OkerekeN.A., Ekpunobi A.JJournal of Non Oxide Glasses **2**, 31-36. .(2011).
[12] Scitz R., Ultrafast Dynamics Quantum Syst., **372**: 674-674. (2002),
[13] Theye M., In Optical properties of thin films, K.L. Chopra and L.K. Malhota, eds, thin film technology and Applications. Tata McGraw – Hill, New Delli, 163. (1985).
[14] Wang, C., X.F. Qian, W.X. Zhang, X.M. Zhang, Y. Xie and Y.T. Qian, Mater. Res. Bull., **34**: 1637-1641 (1999).

[15] Shimizu, A., S. Chaisitsak, T. Sugiyama, A. Yamada, M. Kongai, Thin Solid Films, 361-362, 193-197 (2000).
[16] Jasenek, A., R. Rau, V. Nadenau and H.W. Schock, J. Applied Phys.,**87,** 43-47 (2000).
[17] Chaisitsak, S., Y. Tokita, H. Miyazaki, R. Mikami, A. Yamada, M. Kongai, Buffer layer in Cu(InGa)Se2 solar cells and modules. Proceedings 17th European Photovoltaic Solar Energy Conference, (EPSEC'01), Munich Germany.1011. (2001).
[18] Osuji, R.U., Nig. J. Solar Energy, **14**, 90-99. (2003).
[19] Von-Roedern, B., G.H. Bauer,(1999). Material requirements for buffer layers used to obtain solar cells with high open circuit voltages. National Renewable EnergyLaboratory/CP-520, 26363 Proceedings of Material Research Society™s Spring Meeting, San Francisco, CA, April 6-10, 1999
[20] Naciri, R., H. Bihri, A. MZerd, A. Rahioui, M. Abd-Lefdil and C. Messaoudi, The role of CdS buffer layer in the CuInS₂ thin film solar cell. Revue des Energies Reneouvelables CER 07 Oujda.165-168. (2007).