Optical Properties Of Electrodeposited Zinc Selenide Films On Conducting Glass

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Abstract— **Zinc Selenide (ZnSe) thin films have been successfully deposited on conducting glass substrates using electrodeposition method under direct voltage of 3V at different time intervals. Optical characterization of the film showed low absorption at low photon energy and high absorption at high photon energy with a value of 0.31. The absorbance of the deposited films is shown to depend on the deposition time, which increased with increased time. The energy band gaps of 3.0eV, 2.7eV and 2.8eV were recorded at deposition times of 30secs, 60secs and 90secs respectively with a corresponding increase in the thickness of the deposited films. XRD pattern of the films deposited are indexed to wurzite (hexagonal) crystal structure. Investigation reveals that the grain size of the deposited ZnSe thin films increases with the deposition time**.

> *Keywords—ITO, XRD, UV-VIS, Spectroscopy, Absorbance, Energy band gaps*

I. INTRODUCTION

In recent years, there has been considerable interest in the use of thin films in solar cells. Extensive research has been devoted to grow various kinds of semiconductor thin films. Among various semiconductor films, ZnSe has been identified as a potential material for device applications. ZnSe an important II-VI direct band gap semiconductor has attracted considerable attention due to its uses in light emitting diode, photovoltaic cell, photo detectors, full colour display, tuneable mid – IR laser sources and short wavelength lasers [1], [2], [3], [4], [5], [6]. ZnSe is also attractive host for the formation of doped nanocrystals [7], [8], [9]. Several novel applications have been presented which require size, shape and phase control of ZnSe nanostructured materials [10], [11], [12], [13]. Dimensionality, size and size distribution are known to play important roles in determining the physical and chemical properties of ZnSe thin film materials [14]. Because of the novel properties and various potential applications, ZnSe thin film materials, with typical grain size less than 10nm are attracting increasing attention from researchers all over the world [15]. Thin film materials with grain size less than 10nm exhibit properties that are often superior and sometimes completely new, in comparison with those of conventional coarse grained

materials because of their small size and consequently the large volume fraction of atoms in or near the grain boundary [15], [16]. There are several reports describing various synthesis route for ZnSe nanoparticles [17], [18], [19], [20], [21], [22], [23], [24], [25], [26], [27] most of the reports yielded the cubic (Zinc blende) structure of ZnSe with a less amount of hexagonal (Wurtzite) structure. ZnSe films have been synthesized by various methods such as chemical bath deposition method, pulse laser deposition, electrodeposition method, electron beam evaporation technique, vacuum evaporation, thermal evaporation, molecular beam epitaxy and successive ionic layer adsorption and reaction [28], [29], [30], [31], [32]. Herein we reported electrodeposition method owing to its many advantages like rapidity, free from porosity, high purity, industrial application, potential to overcome shape limitations or allows the production of free- standing parts with complex shapes, higher deposition rates, produce coatings on widely different substrates, ability to produce composition unattainable by other techniques, the possibility of forming simple low cost multilayers in many different systems, and no postdeposition treatment amongst others [15].

II. EXPERIMENTAL

All reagents were used as purchased and solvents were distilled prior to use. ZnSe films were deposited on indium doped tin oxide, ITO, (conducting glass) by electrodeposition method. The electrodeposition bath system is composed of Zinc tetraoxosulphate VI Heptahydrate ($ZnSO_4.7H_2O$) as source of cation (Zn^{2+}), Selenium IV Oxide (SeO_2) as source of anion (Se^{2-}), Tetra-oxo Sulphate VI acid (H_2SO_4) as pH control, Potassium tetraoxo Sulphate VI (K_2SO_4) as inert electrolyte and distilled water.

A. Preparation of solution

0.14M solution of $ZnSO_4.7H2O$ was prepared by dissolving 20g of it in 500ml of distilled water and it dissolved completely. 0.054M solution of SeO_2 was prepared by dissolving 3g of it in 500ml of distilled water and when thoroughly shaken, it dissolved completely in water with clear solution. Again 0.1M solution of H_2SO_4 was prepared by dissolving 3ml of it in 500ml of distilled water and it dissolved completely. Finally 0.092M of K_2SO_4 was prepared by dissolving

8g of it in 500ml of distilled water and it dissolved completely with a clear solution

B. Electrodeposition

Deposition of ZnSe on ITO substrate was carried out using electrodeposition technique. 28ml, 28ml, 5ml, and 4ml solutions of $ZnSO_4.7H_2O$, SeO_2, H_2SO_4, and K_2SO_4 respectively were measure in 100ml beaker and stirred to achieve uniformity and the resultant solution was used for the deposition.
The substrate ITO was used as the cathode while a copper electrode was used as the anode. The deposition was done under 3V at room temperature (26^oC) and the pH was maintained at 1.8 for 30secs. The same process was repeated for 60 and 90secs. The possible reaction mechanism is shown below:

$$Zn^{2+} + 2e^- \rightarrow Zn$$

$$SeO_2 + H_2O \rightarrow H_2SeO_3$$

$$H_2SeO_3 + 4H^+ + 4e- \rightarrow Se + 3H_2O$$

$$Zn + Se \rightarrow ZnSe$$
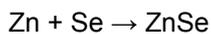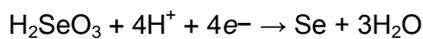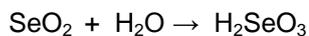
At the end of deposition, the coated substrates were washed well with distilled water and air dried at room temperature. The deposited films were taken for structural characterization using Cu-Kα (λ = 0.154nm) on an MD-10.3 diffractometer. The samples were mounted flat and scanned between 10° and 80° in a step size of 0.05 and with a count rate of 9s. Absorbance spectra data of the films were obtained using Janway 6405 UV- visible spectrophotometer in the wavelength range of 200nm – 900nm. From the absorbance, various other parameters which include: Transmittance, Reflectance, Refractive index, Optical thickness, Coefficient of absorption, Extinction coefficient, Optical conductivity and dielectric constants were derived

III. RESULTS AND DISCUSSION

Figure 1 shows the variation of optical absorbance of the films deposited, at different time interval, with photon energy. This variation reveals low absorption in the lower photon energy (VIS-IR region) with value of 0.09, 0.13 and 0.14 for the film deposited at 30secs, 60secs and 90secs respectively. The absorbance tends to be high in the high photon energy (UV region) with a value of 0.20, 0.28 and 0.31 for the film deposited at 30secs, 60secs and 90secs respectively. This absorbance is also a function of the thickness as seen in the calculated optical thickness plotted in figure 2. The high absorbance in the UV region makes ZnSe useful in forming p – n junction solar cells with other suitable thin film materials for photovoltaic applications [29] and a good window layer for solar cell application [30]. The low absorption of energy makes ZnSe films useful for optical components in higher laser window and multispectral applications, proving good imaging characteristics [33]. Figure 3 shows the spectral transmittance (%) of the films. The

transmittance spectra reveal transmission of above 50% in the UV region for all the films and about 80% in the near infra-red region for all the films. The higher transmittance in the visible region makes it a strong candidate for use in opto-electronic devices [31], [34], [35], [36], [37]. The wide transmission range of ZnSe film makes the material useful in manufacturing optical components, windows, mirrors, and lenses for high power IR laser [38]. Figures 4-6 show the plot of absorption coefficient squared (α^2) versus photon energy of ZnSe films deposited at 30secs, 60secs and 90secs respectively. The linear dependence showed by α^2 and photon energy indicates that the transition is direct. The energy gaps were found to be 3.1eV, 2.8eV and 2.7eV for the film deposited at 30secs (thickness of 101nm), 60secs (thickness of 180nm) and 90secs (thickness of 258nm) respectively. The observed increase in the energy gap as the thickness increased is as a result of quantum confinement size effect in line with Heisenberg uncertainty principle and discretization of continuous energy bands as the thickness decreases [39], [40]. The refractive index of the deposited ZnSe films were calculated and plotted. **Figure 7** showed that the refractive index increased with the deposition time and as well as the thickness of the films. The figure display a high refractive index with range of 2.0 – 2.5 for all the films. The extinction coefficient of the films was estimated using the formula $k = \frac{\alpha\lambda}{4\pi}$ figure 8 whereas the optical conductivity was estimated using $\sigma_0 = \frac{\alpha n c}{4\pi}$ figure 9. Figures 8-9 showed that both the extinction coefficient and optical conductivity increased with the deposition time. The figures as showed that the films have least absorption in the lower energy level, (VIS-IR region) but very high rate of absorption in the high energy level (UV region). These optical properties makes ZnSe thin films nice glazing materials for maintaining cool interior in buildings in warm climate regions while still keeping the rooms well illuminated.
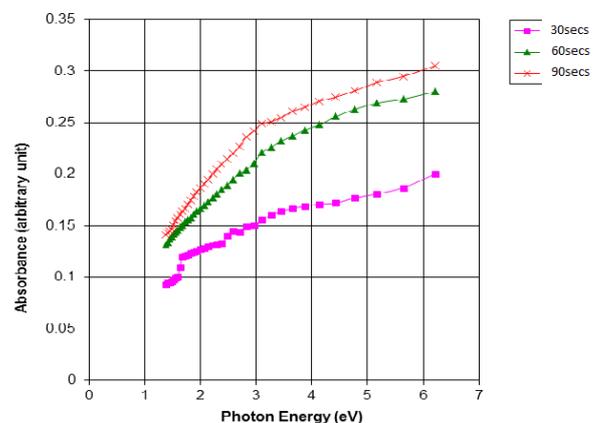
Figure 1: *Spectral absorbance of ZnSe films deposited at different time interval.*
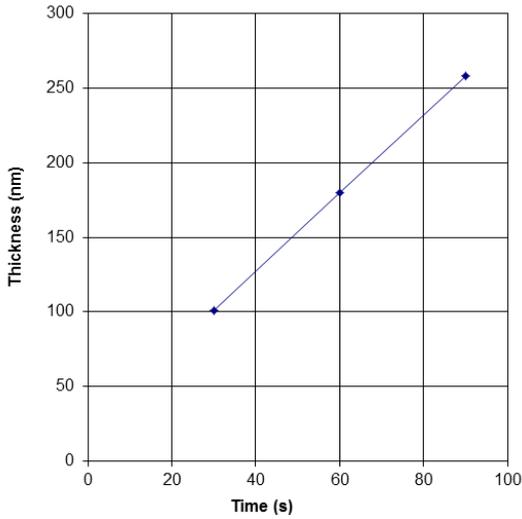
Figure 2: *Plot of the thickness of the deposited films versus time.*
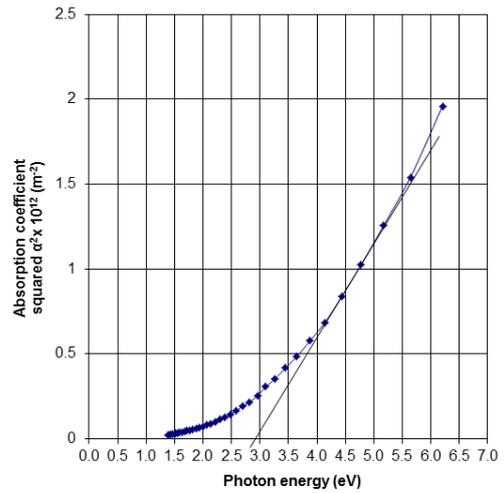
Figure 5: *Plot of α^2 versus photon energy of ZnSe film deposited at 60secs*
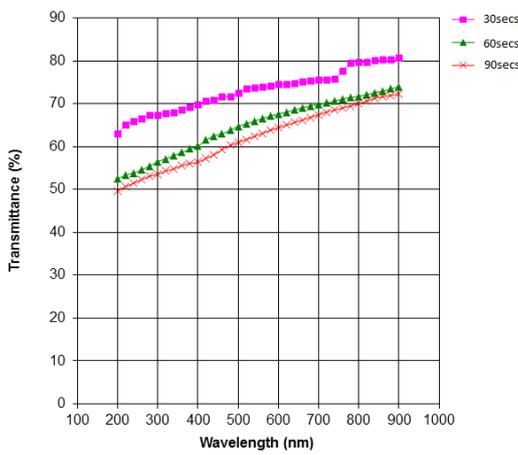
Figure 3: *Spectral transmittance of ZnSe films deposited at different time interval.*
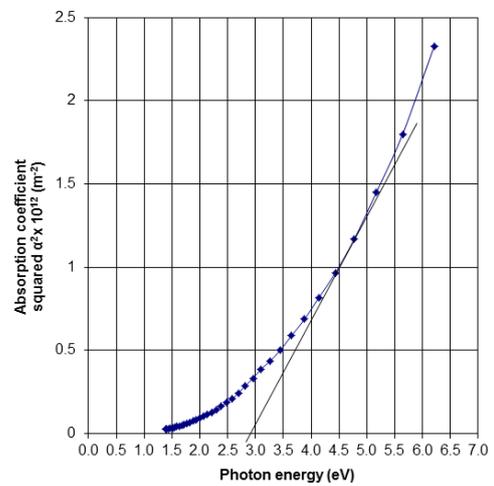
Figure 6: *Plot of α^2 versus photon energy of ZnSe film deposited at 90secs*
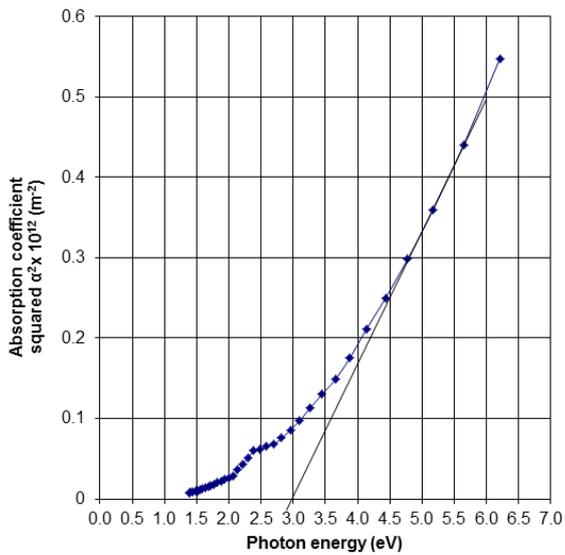
Figure 4: *Plot of α^2 versus photon energy of ZnSe film deposited at 30secs*
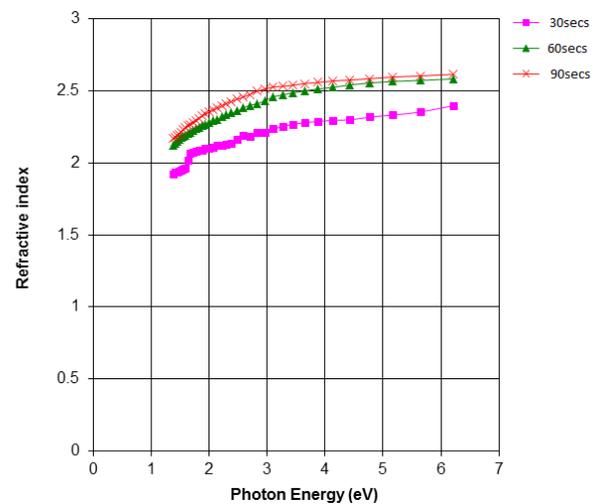
Figure 7: *Plot of refractive index versus photon energy for the films deposited at 30, 60 and 90secs*
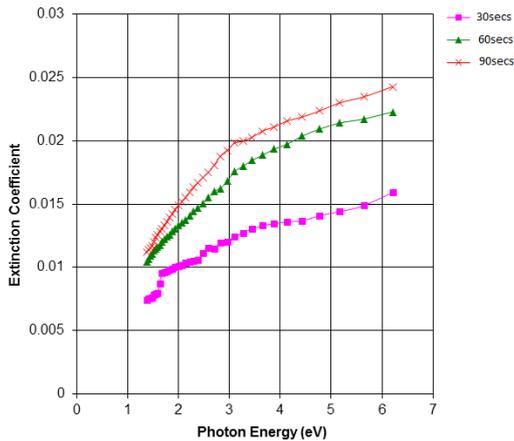
Figure 8: *Plot of extinction coefficient versus photon energy for the films deposited at 30, 60 and 90secs*
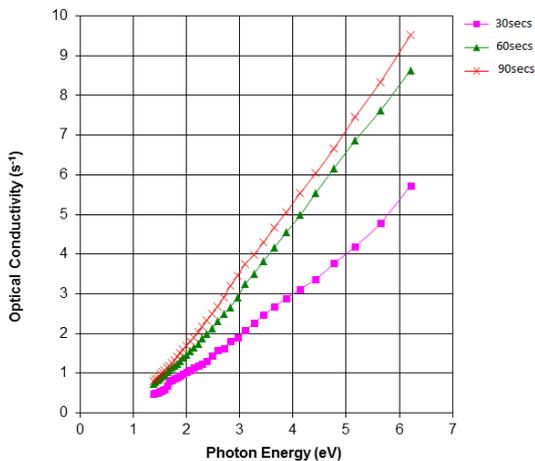
Figure 9: *Plot of optical conductivity versus photon energy for the films deposited at 30, 60 and 90secs*.

Figure 10: *X-ray diffraction pattern of ZnSe thin film deposited on conducting glass (ITO) substrate for 30secs under optimum experimental conditions*
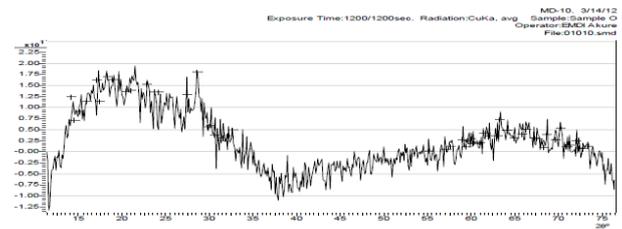
Figure 11: *X-ray diffraction pattern of ZnSe thin film deposited on conducting glass (ITO) substrate for 60secs under optimum experimental conditions*
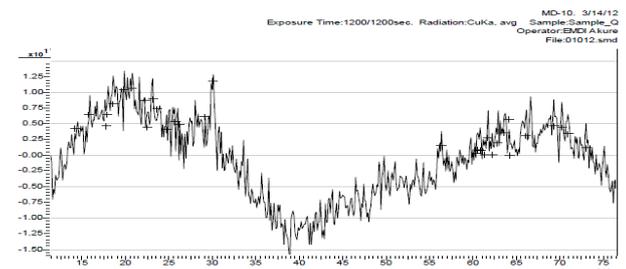
Figure 12: *X-ray diffraction pattern of ZnSe thin film deposited on conducting glass (ITO) substrate for 90secs under optimum experimental conditions*

Figures 10 – 12 showed the XRD pattern of the deposited films under the experimental optimum conditions for 30secs, 60secs and 90secs respectively. The observed diffraction peaks in these patterns can be indexed to wurzite (hexagonal) structure. The several peaks of hexagonal phase of ZnSe have been obtained due to diffraction from (002), (101), (110), (103), (112), (202), (203), (210) and (105) planes of ZnSe. The calculated grain size increased with the deposition time and the average crystalline grain size of 1.55Å, 2.40Å and 2.88Å were obtained at deposition time of 30sec, 60sec and 90secs respectively, and this showed that crystalline size of the deposited films increased with deposition time

IV. CONCLUSION

ZnSe films have been successfully deposited using electrodeposition technique under direct voltage of 3V. Optical characterization of the deposited films showed that, ZnSe films have low absorption in the VIS – IR region and the absorption tends to be high at high photon energy (UV region). The calculated optical energy band gap showed that energy band gap increased with decrease in crystalline size and thickness which is as a result of quantum confinement size effect. XRD pattern of the deposited films showed that hexagonal polycrystalline structures of ZnSe thin films were formed.

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