Effect of Applied Voltage on Optical Properties of Zinc Selenide Thin Films Deposited on Conducting Glasses

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Zinc Selenide (ZnSe) has been deposited on conducting glass substrate using the electro-deposition method. The effect of increase voltage on optical properties of the deposited film was studied using Janway 6405 UV-visible spectrophotometer. The result obtained from UV-visible spectrophotometer film showed high absorption at high photon energy with a range value of 0.28-0.37 and low absorption at low photon energy, which is dependent on the deposition voltage. The optical thickness of films was calculated using a relation between thickness, transmittance, absorption coefficient, and reflectance. Optical thicknesses of 180nm, 200nm and 228nm were calculated for these films deposited under 3V, 4V and 5V, respectively. Also, refractive indices of films were calculated from their reflectance. The result showed that high refractive index of 2.8 was recorded for all films and energy gap of 2.8eV was also calculated for all the films. The structural characterization of the films was done using Cu-Kα (λ = 0.154nm) on an MD-10.3 diffractometer. XRD of the deposited films, from the XRD pattern, showed hexagonal crystal structure with the average crystalline grain sizes of 4.95Å, 2.30Å and 0.82Å under deposition voltage of 3V, 4V and 5V, respectively.

1. Introduction

Zinc selenide (ZnSe) is an interesting II-VI semiconductor material that has attracted considerable attention owing to its wide applications. ZnSe has large band gap of 2.7eV at room temperature and can be used in laser diodes, green-blue light emitting diodes and solar cells [1]. ZnSe is also a good candidate for optically controlled switching due to its low absorptivity at infrared wavelength, giant photoresistivity and visible transmission [1,2]. It is also a promising material for windows, lenses, output couplers and beam expanders [2]. Dimensionality, size and size distribution are known to play important roles in determining the physical and chemical properties of ZnSe thin film materials [3]. ZnSe thin film materials, with typical grain size less than 10nm are attracting increasing attention from researchers all over the world because of their novel properties and various potential applications [4]. Thin film materials with grain size less than 10nm exhibit properties that are often superior and sometimes completely new in comparison to 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 [4,5]. There are several reports describing various synthesis route for ZnSe nano-particles, most of the reports yielded the cubic (Zinc blende) structure of ZnSe with less amount of hexagonal (Wurtzite) structure [6-16]. ZnSe films have been synthesized by various methods such as chemical bath deposition, self-catalytic liquid solid growth, microwave irradiation technique, pulsed laser deposition, molecular beam epitaxy, metalorganic chemical vapor deposition, solvothermal and organometallic vapor phase epitaxy [17-22]. Herein we report the electro-deposition method owing to its many advantages like rapidity, free from porosity, high purity, industrial application, potential to overcome shape limitations and 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 multi-layers in many different systems, and no post deposition treatment amongst others [4]. The effect of voltage on the optical properties of the electrodeposited films was also studied.

2. Experimental Set Up

All reagents were used as purchased and solvents were distilled prior to use. ZnSe films were deposited on conducting glass indium doped tin oxide (ITO) by electro-deposition method. Prior to

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their use the substrates were cleaned with detergent solutions, rinsed with distilled water and then rinsed with acetone, methanol and distilled water, and dried before use. An area of about 6.00cm^2 of the substrate was dipped into the electrolyte (solution). The substrate ITO was used as the cathode while a copper electrode was used as the anode, as shown in Fig. 1. The anode and cathode were of the same length (4cm each) and separated by a distance of 10cm. The electro-deposition bath system is composed of Zinc tetraoxosulphate VI Heptahydrate ($ZnSO_4.7H_2O$) as the source of cation (Zn^{2+}), Selenium IV Oxide (SeO_2) as the source of anion (Se^{2-}), Tetra-oxo Sulphate VI acid (H_2SO_4) for pH control, Potassium tetraoxo Sulphate VI (K_2SO_4) as an inert electrolyte, and distilled water as the solvent.

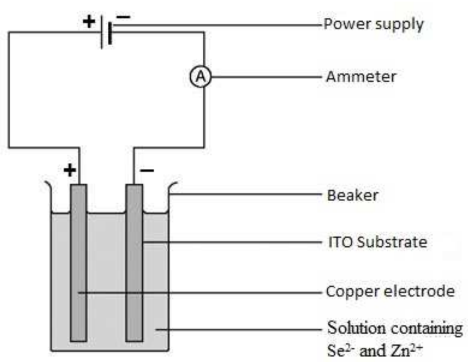

Fig.1: Experimental set up.

2.1. Preparation of solution

0.14M solution of $ZnSO_4.7H_2O$ was prepared by dissolving completely 20g of it in 500ml of distilled water. 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.

2.2. Electro-deposition

Deposition of ZnSe on the ITO substrate was carried out using electro-deposition technique. 28ml, 28ml, 5ml, and 4ml solutions of $ZnSO_4.7H_2O$, SeO_2, H_2SO_4, and K_2SO_4, respectively, were measured 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 and a copper electrode was used as the anode. The deposition was done under 3V at room temperature (26^{o}C) and the pH was maintained at 1.8 for 60secs. The same process was repeated for 4V and 5V and in each case there was good film deposition.

The possible reaction mechanism is shown below as

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

$$SeO_2 + H_2O \rightarrow H_2SeO_3$$

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

$$Zn + Se \rightarrow ZnSe$$

At the end of deposition process the coated substrates were washed well with distilled water and air dried at room temperature. The thickness of the deposited films was determined gravimetrically. 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^o and 80^o 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 calculated.

3. Results and Discussion

The optical absorbance of the deposited films under different direct voltages is shown in Fig. 2. The film reveals low absorption in VIS-IR region with value of 0.12 – 0.15 for the films deposited under various voltages (3V, 4V and 5V) and high absorption in UV region with value of 0.28 – 0.37. Again, it is observed from Fig. 2 that the absorbance of the film deposited under 5V lies below that obtained under 4V in the photon energy range of 3.45eV – 5.52eV. This observation might be attributed to quantum size confinement as a result of the drastic decrease in the crystallite size (0.082nm) of the film deposited under 5V as seen in the XRD result. 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 [18] and a good window layer for solar cell application [19]. The calculated optical thickness shows that there is an increase in the thickness of deposited films as the deposition voltage is increased Fig. 3. The plot of the spectral transmittance (%) of the deposited films versus wavelength is shown in Fig. 4. The transmittance spectra reveal transmission between 43% – 53% in the UV region for all films and between 70% – 73% 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 [20,23-26]. The wide transmission range of ZnSe film makes the material useful in manufacturing optical components, windows, mirrors, and lenses for high power IR laser [27]. Fig. 5 shows the plot of the refractive index versus photon energy. The figure displays a high refractive index in the range of 2.1 – 2.7 for all films. It is also observed that the applied voltage has insignificant effect on the refractive index of these films. Figs. 6 and 7 show the plot of extinction coefficient versus photon energy and optical conductivity versus photon energy, respectively. Both the extinction coefficient plot and optical conductivity plot were estimated using the formulae $\mathbf{k} = \frac{\alpha\lambda}{4\pi}$ and $\sigma_0 = \frac{\alpha nc}{4\pi}$ respectively, where $\mathbf{k}$ is the extinction coefficient, σ_0 is the optical conductivity, **c** is the speed of light, **n** is the refractive index, λ is the photon wavelength, and α is the coefficient of absorption. The figures 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 mostly in warm climate regions while still keeping the rooms well illuminated.

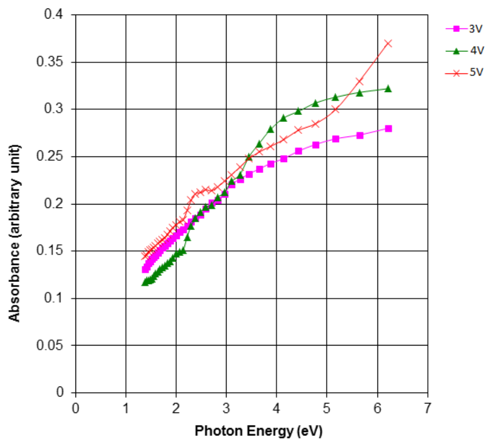

Fig.2: Spectral absorbance of ZnSe films deposited at different voltages.

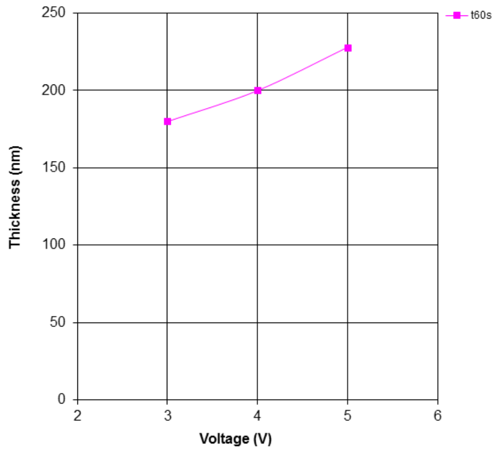

Fig.3: Plot of the thickness of the deposited films versus voltage.

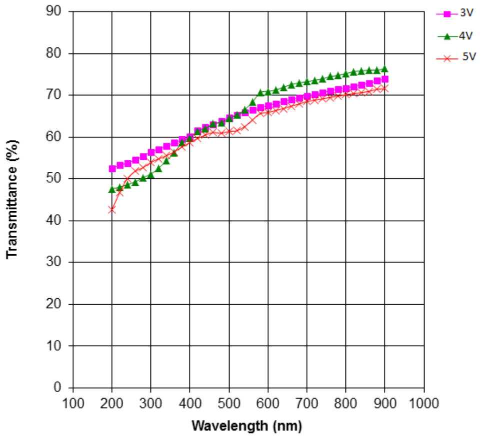

Fig.4: Spectral transmittance of ZnSe films deposited under 3V, 4V and 5V.

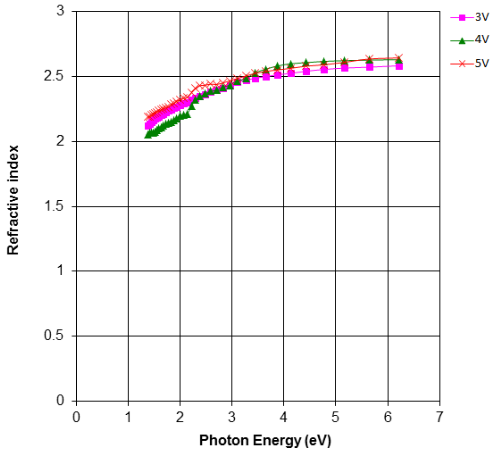

Fig.5: Plot of refractive index versus photon energy for the films deposited under 3V, 4V and 5V.

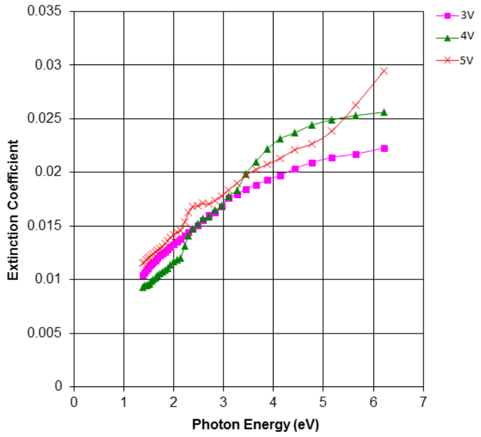

Fig.6: Plot of extinction coefficient versus photon energy for the films deposited under 3V, 4V and 5V.

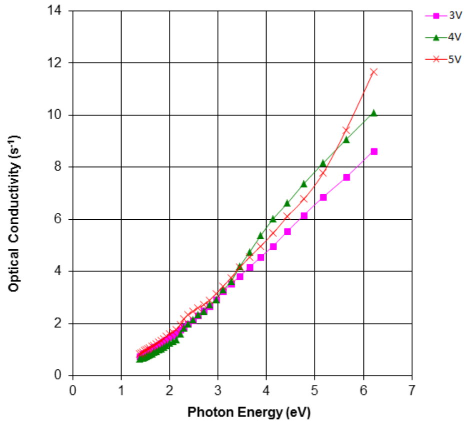

Fig.7: Plot of optical conductivity versus photon energy for the films deposited under 3V, 4V and 5V.

Figs. 8-10 show the plot of absorption coefficient squared ($\boldsymbol{\alpha}^2$) versus photon energy of ZnSe films deposited under direct voltage of 3V, 4V and 5V, respectively. The linear dependence showed by $\boldsymbol{\alpha}^2$ and the photon energy indicates that the transition is direct. The energy gap was found to be 2.8eV for all films, but the thickness of the deposited film increased with the deposition voltage. Figs. 11-13 show the XRD pattern of the deposited films under optimum experimental conditions under 3V, 4V and 5V, 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 decreased with increased voltage and the average crystalline grain size of 4.95Å, 2.30Å and 0.82Å were obtained under deposition voltage of 3V, 4V and 5V, respectively.

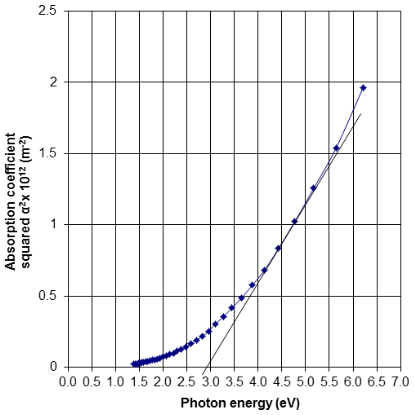

Fig.8: Plot of $\boldsymbol{\alpha}^2$ versus photon energy of ZnSe film deposited under direct voltage of 3V.

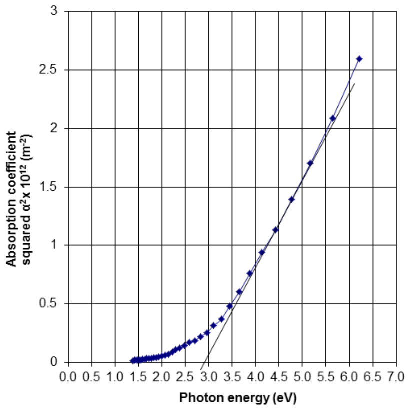

Fig.9: Plot of $\boldsymbol{\alpha}^2$ versus photon energy of ZnSe film deposited under direct voltage of 4V.

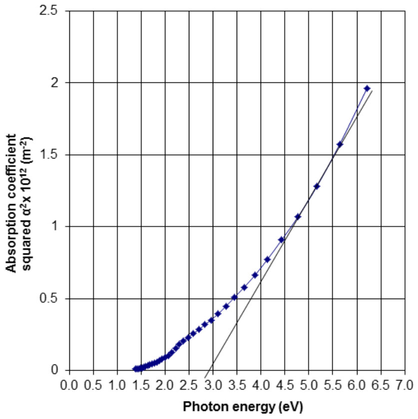

Fig.10: Plot of $\boldsymbol{\alpha}^2$ versus photon energy of ZnSe film deposited under direct voltage of 5V.

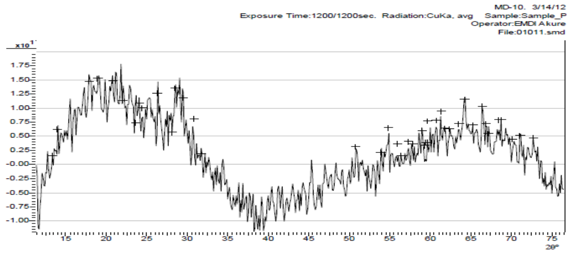

Fig.11: X-ray diffraction pattern of ZnSe thin film deposited under direct voltage of 3V.

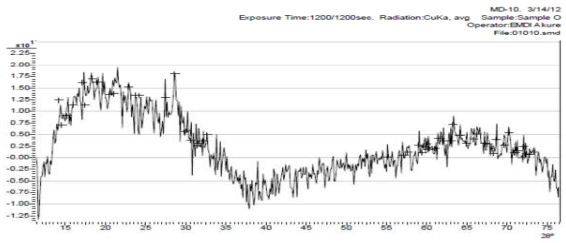

Fig.12: X-ray diffraction pattern of ZnSe thin film deposited under direct voltage of 4V.

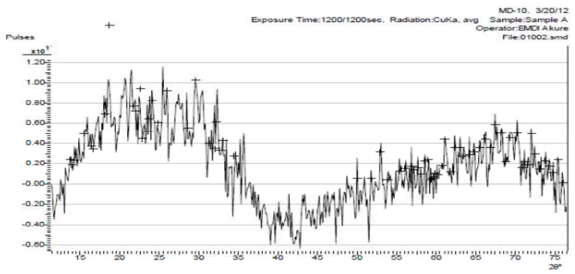

Fig.13: X-ray diffraction pattern of ZnSe thin film deposited under direct voltage of 5V.

4. Conclusion

Electro-deposition technique has been used to deposit poly-crystals of ZnSe thin film on glass substrate under different direct voltages. The optical characterization of deposited films showed that the absorbance, optical thickness, transmittance, extinction coefficient and optical conductivity are affected by the voltage change whereas refractive index and the band gap were not affected by the voltage change. XRD pattern of the deposited film showed hexagonal crystalline structure with decreased grain size as the deposition voltage increased.

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