Influence Of Supporting Electrolyte On The Structural And Optical Properties Of Zinc Selenide Thin Films

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Abstract
Thin films of ZnSe have been synthesized by electrodeposition technique. XRD analysis showed that the ZnSe thin films, deposited, exhibit cubic structure with a preferred orientation along (111) plane. All deposited films exhibited absorption value between 0.006-0.356 a.u in both regions with wavelength of 300-900 nm. It is observed that the absorbance of the films is as high as 0. 35a.u in visible & infrared regions. The sample A deposited at 30s recorded the highest absorbance value of about 0. 35a.u with a wavelength of 440nm and the sample B deposited at 35s recorded the absorbance value of about 0.24 a.u with wavelength of 320 nm. Sample C deposited at 40s recorded the lowest absorbance value of 0.14 a.u with wavelength of 300nm. The transmittance of the films is as high as 47-94% in visible & infrared regions. Both of them have peak transmittance in infrared region. The sample A deposited at 30s recorded the lowest value of about 84% of transmittance while the sample B deposited at 35s recorded the highest transmittance value of about 94%. The sample A deposited at 30s recorded the highest reflectance value of about 0.203% with a wavelength of 300 nm and the sample B deposited at 35s recorded the reflectance value of about 0.172% with wavelength of 300nm. Sample C deposited at 40s recorded the lowest reflectance value of 0.14% with wavelength of 300 nm.The optical band gap energy was 2.5-2.2 eV.

Index Terms: ZnSe, thin films, electrodeposition, structural and optical properties

1.0 Introduction

ZnSe is a chalcogenide material which has been proved to be one of the two compounds that can be prepared in both n and p type forms [1]. Due to its particular characteristics, such as non linear optical properties, photoluminescent and electroluminescent properties [2], [3]. ZnSe has become a promising material in many applications: it is suitable for red, blue and green light emitting diodes, thin film transistors, infrared coating material, photoelectrochemistry, laser screens, n type window layer thin film herterojunction, solar cells, photodetector, ultrasonic transducers [4], [5]. ZnSe films has been prepared by various growth techniques, including Molecular beam deposition, reactive evaporation, chemical deposition, Atomic layer deposition, electron beam evaporation, electrochemical deposition, Pulsed laser deposition and chemical bath deposition [6], [7]. Zinc selenide (ZnSe) is a wide band gap II-VI semi-conductor and has attracted considerable attention for its wide range of applications in various optoelectronic devices and in solar cells. It is a direct band gap semiconductor and is transparent over wide range of visible spectrum. Polycrystalline ZnSe thin films have been identified as suitable material for electroluminescent display and window layers in solar cells. In recent years efforts have been devoted to develop blue green laser diodes based on ZnSe and its alloys. So far these have not been realized, mainly because of the difficulty in controlling electrical conductivity. Preparation of conductor layer is essential for its use as light emitting devices. As in other large band gap semiconductor systems, progress in ZnSe was hindered by lack of shallow dopant source, essentially acceptors [8]. ZnSe is an important semiconductor material with a large band gap, which has a vast potential use in thin films devices and as n-type window layer for thin film herterojunction solar cells [9].

In this research work we reported on influence of supporting electrolyte on the structural and optical properties of zinc selenide thin films, in order to study kind of transitions on the structural and optical properties

Experimental details

2.1 Materials and Methods

The chemical used for the syntheses were analytical grade which included Zinc Tetraoxosulphate VI Heptehydrate (ZnSo4.7H2O), Selenium IV Oxide (SeO_2), Potassium tetraoxosulphate VI (K_2SO_4), and H_2SO_4. Electrochemical deposition technique (EDT) was used in this work which involves the deposition of any substance on an electrode as a result of electrolysis which is the occurrence of chemical changes owing to the passage of electric current through an electrolyte. This process involves oriented diffusion of charged growth species through a solution when an external field is applied and reduction of charged growth species at the growth or deposition which also serves as an electrode.

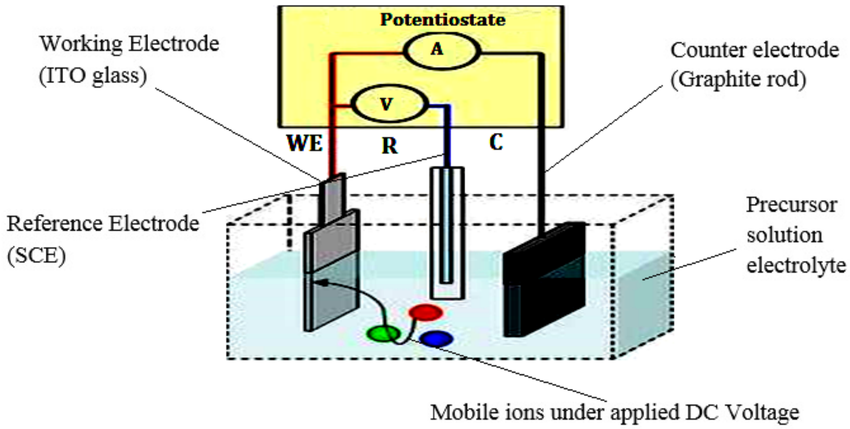

Fig.1: Schematic Diagram of Electrodeposition Setup

2.2 Substrate cleaning procedure

Transparent Indium doped tin oxide (ITO) coated glass substrates with a sheet resistance of about 14.42Ω/m was used as substrate for deposition. The glass substrates were coated only on one side and this conducting side of the glass was detected by the use of a digital multimeter which gave reading as the non-conducting side does not give any reading for the deposition of thin films materials. Hand gloves were used to handle the substrates to avoid contamination. The substrates were dipped in acetone, methanol, rinsed with distilled water and later ultrasonicated for 30min in acetone solution after which they were rinsed in distilled water and kept in an oven at to dry. All the prepared substrates were kept in air-tight container

2.3 Synthesis of zinc selenide thin films

The syntheses of zinc selenide thin films materials were carried out using the cationic precursor which was an aqueous solution of of 1mol of Zinc Tetraoxosulphate VI Heptehydrate (ZnSO4.7H2O) while the anionic precursor of 1mol of selenium IV Oxide (SeO_2) solution. This was to ensure uniform deposition. The electrodeposition bath system is composed of a source of cation (ie ZnSO4.7H2O for Zn^{2+}), a source of anion (i.e SeO_2 for Se^{2-}), distilled water all in 100ml beaker, magnetic stirrer was used to stir the reaction bath. A power supply was used to provide electric field (DC voltage), a Indium doped Tin Oxide (ITO) was used as the cathode while the anode was carbon and fluorine electrode. The temperature was kept constant and the growth of ZnSe thin films was carried out varying the deposition time (30-40s) and pH (1.9) in order to determine the optimum condition for the deposition of ZnSe thin films others bath parameter were determined with respect to the different bath parameters which includes temperature and voltage of deposition and substrate for the deposition, the concentration of the solution were kept constant throughout the experiment. The concentration of the compounds was maintained as prepared. 20cm^3 each of $ZnSO_4.7H_2O$ and (SeO_2) was measured into 100ml beaker using burette. 5cm^3 of K_2SO_4 and H_2SO_4 was measured into the same 100ml beaker containing $ZnSO_4.7H_2O$ and (SeO_2) respectively to serve as the inert electrolyte which helps to dissociate the Zn from the $ZnSO_4.7H_2O$ and Se from the (SeO_2) to form the required ZnSe film on the substrate. The entire mixture was stirred with the magnetic stirrer to achieve uniformity. In each of the reaction baths prepared, a substrate (ITO) and carbon and fluorine electrode were connected to a DC power supply source.

2.4. Characterization technique

The synthesized films were characterized for their optical properties, electrical properties, Scanning electron microscope and structural properties. The structural properties were obtained using X- Ray Diffractometer (XRD) analysis was carried out using DM-10 diffractometer for the 2θ ranging from 15- 53 with {cukal} (λ = 1.540598Ǻ) radiation. Optical absorbance study was carried out using M501 UV-Visible spectrophotometer. The films coated with Indium Tin Oxide glass was placed across the sample radiation pathway while the uncoated the reference path. The absorption data were manipulated for the determination of band gap energy.

3.0 Theoretical Background

From the law of conservation of energy, we obtained,

$$A+T+R=1$$

Where A is the absorbance, R is the Reflectance, and T is the transmittance, given by

$$T = 10^{-A}$$

Results and Discussion

4.1 Structural Properties of Zinc Selenide Films

The X-ray diffraction patterns of ZnSe thin films are presented in Figure.1-2. The X-ray diffraction patterns show a cubic structure which correspond to 111 planes. These result compare well with the reported values in [10-12] who reported the XRD preferred orientation of (111- 311) planes. [13] reported the preferred orientation in the (111-311) and [14] obtained a film orientation in the (111-222) planes. The diffraction angle 2Θ value is 16.61˚and 15.43^0 with d = 5.337Å and d = 5.742Å. The preferred orientation lies along the (111) plane. The lattice constant was given in the X-ray diffraction analysis is found to be a = 5.6667Å. The crystallite size was determined by means of the X-ray line broadening method using Scherer equation [15]

$$D = \frac{0.94\lambda}{\beta Cos\theta}$$

Where λ is the wavelength of CuKal radiation (λ = 1.540598 Å), is the full width at half ***β*** maximum FWHM of the (hkl) peak of the diffracting angle hkl 2θ. The average grain size D, the dislocation density δ is calculated using the following relation [16], [17]

$$\delta = \frac{1}{D^2} \text{ lines/m}^2$$

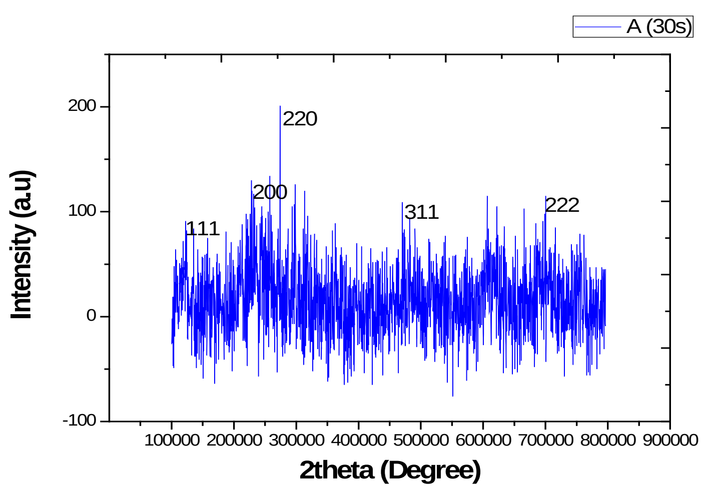

Figure 1. X-ray diffraction pattern of ZnSe film (Sample A 30s)

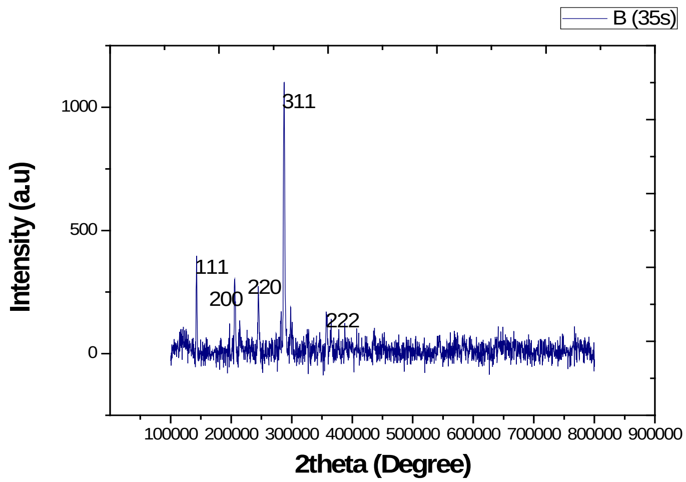

Figure 2. X-ray diffraction pattern of ZnSe film (Sample B 35s)

Table 1. Structural parameters of ZnSe film

Sample Thickness	2θ (degree)	d (spacing) Å	Lattice constant (Å)	(β) FWHM	(hkl)	Grain Size(D) nm	Dislocation density,**σ**
A (30s)	16.61	5.337	5.67	0.25476	111	5.498	0.436
	17.55	5.054		1.2756	200	1.094	2.065
	18.06	4.912		0.00707	220	1.984	0.011
	18.97	4.676		0.4322	311	3.251	0.646
	18.93	4.688		0.18226	222	7.709	0.273
	15.43	5.742	5.67	0.76246	111	1.834	1.407
B (35s)	16.09	5.509		0.76246	200	1.835	1.348
	16.65	5.324		0.76246	220	1.837	1.302
	17.09	5.187		0.76246	311	1.838	1.268
	17.69	5.014		0.76246	222	1.839	1.224

4.2 Optical Properties of ZnSe Films

The optical absorption spectral of ZnSe films deposited at different time (30-40s) at constant voltage (1V) in Figure 3 reveal a very low absorption in the lower VIS-IR regions and high absorption in ultra violet region. All deposited films exhibited absorption value between 0.006-0.356a.u in both region with wavelength of 300-900nm. It is observed that the absorbance of the films is as high as 0.35a.u in visible & infrared regions. The sample A deposited at 30s recorded the highest absorbance value of about 0.35a.u with a wavelength of 440nm and sample B deposited at 35s recorded the absorbance value of about 0.24a.u with wavelength of 320nm. Sample C deposited at 40s recorded the lowest absorbance value of 0.14a.u with wavelength of 300nm. The low absorption value recorded reveal that as the deposition time increase the ions of the supporting electrolyte stop acting which show that supporting electrolyte can fastening the rate of deposition [10], [11], [17].

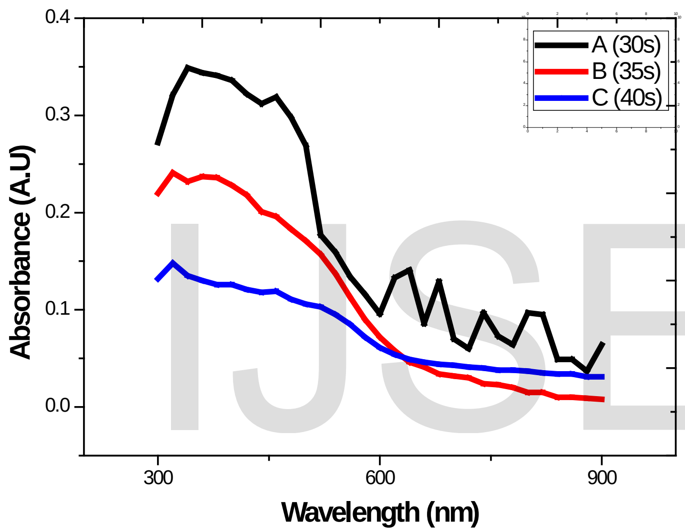

Figure 3. Plot of absorbance versus Wavelength

The optical transmittance spectral of the ZnSe thin films deposited at different time (30-40s) at constant voltage (1V) shown in Figure 4. All deposited films exhibited transmittance between 46% and 84% in the visible region. The transmittance spectra show very high transmittance in the VIS-NIR regions of the electromagnetic spectrum. It is observed that the transmittance of the films is as high as 47-94% in visible & infrared regions. Both of them have peak transmittance in infrared region. The sample A deposited at 30s recorded the lowest value of about 84% of transmittance while the sample B deposited at 35s recorded the highest transmittance value of about 94%. The wide transmission range (47-94%) revealed in the figure makes the materials useful in manufacturing optical components, windows, mirrors, lenses for high power infra red laser and others properties like solar cells fabrication [10], [11], [17].

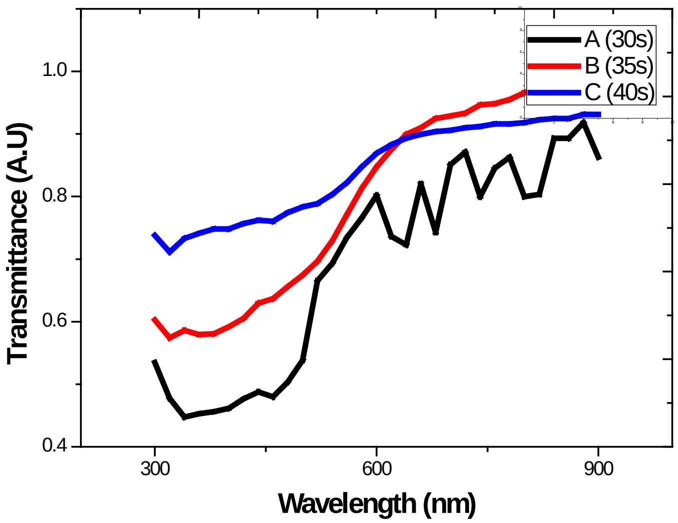

Figure 4. Plot of transmittance versus wavelength

The optical reflectance of ZnSe films deposited at different time (30-40s) at constant voltage (1V) in Figure 5 reveal a very low reflection in the lower VIS-IR regions due to the influence of the supporting electrolyte. All deposited films exhibited absorption value between 0.005-0.203% in both regions with wavelength of 300-900nm. It is observed that the reflectance of the films is as high as 0.203% in visible & infrared regions. The sample A deposited at 30s recorded the highest reflectance value of about 0.203% with a wavelength of 300nm and the sample B deposited at 35s recorded the reflectance value of about 0.172% with wavelength of 300nm. Sample C deposited at 40s recorded the lowest reflectance value of 0.14% with wavelength of 300nm. The low reflectance value recorded reveal that as the deposition time increase the ions of the supporting electrolyte stop acting which show that supporting electrolyte can fastening the rate of deposition [10], [11], [17].

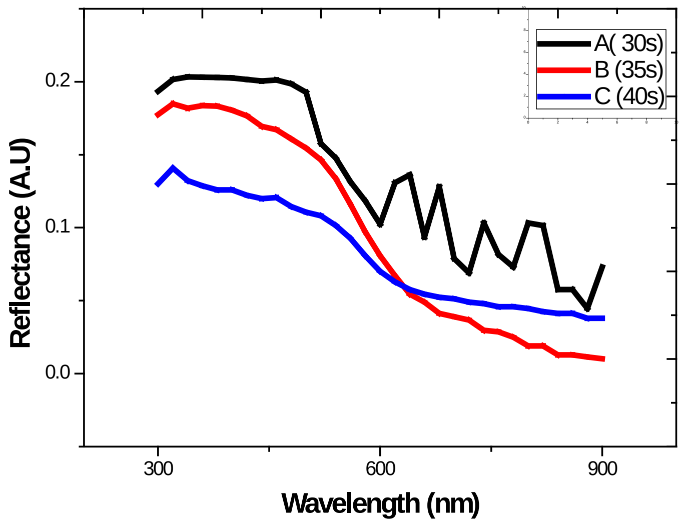

Figure 5. Plot of reflectance versus wavelength

Optical absorbance measurements were made on the films deposited on conducting glass substrates in the wavelength range 300 – 900nm at room temperature to ascertain the nature of the band gap. Substrate absorption, if any was corrected by placing an identical uncoated Tin Oxide substrate in the reference path. The band gap of the films was determined by plotting a graph between absorption coefficients as a function of photon energy. Extrapolation of the linear region to the photon energy axis gives the band gap of the material. Figure 6 show the absorption coefficient as a function of photon energy graph for the films deposited at different time interval. The plots are linear, extrapolation of the plot to the photon energy axis yields the band gap in the range of 2.3 – 2.0eV for the films deposited at different deposition time interval [10], [11], [17].

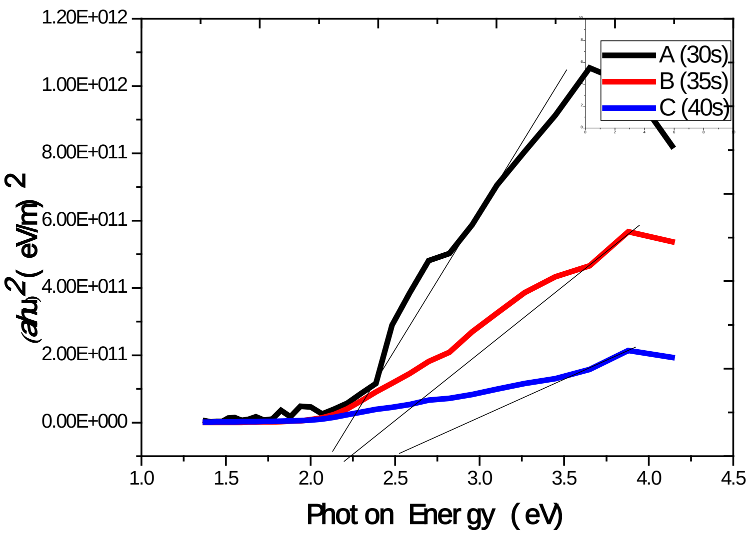

Figure 6. Plot of absorption coefficient square versus Photon Energy

5.0 Conclusion

ZnSe thin films have been successfully prepared by electrodeposition technique. The obtained value of the optical energy gap was 2.3-2.2eV; the relations indicate direct transitions. XRD analysis showed that the ZnSe thin films, deposited, exhibit cubic structure with a preferred orientation along (111) plane. All deposited films exhibited absorption value between 0.006-0. 356a.u in both regions with wavelength of 300-900nm. It is observed that the absorbance of the films is as high as 0. 35a.u in visible & infrared regions. The sample A deposited at 30s recorded the highest absorbance value of about 0. 35a.u with a wavelength of 440nm and the sample B deposited at 35s recorded the absorbance value of about 0. 24a.u with wavelength of 320nm. Sample C deposited at 40s recorded the lowest absorbance value of 0.14a.u with wavelength of 300nm. The transmittance of the films is as high as 47-94% in visible & infrared regions. Both of them have peak transmittance in infrared region. The sample A deposited at 30s recorded the lowest value of about 84% of transmittance while the sample B deposited at 35s recorded the highest transmittance value of about 94%. The sample A deposited at 30s recorded the highest reflectance value of about 0.203% with a wavelength of 300nm and the sample B deposited at 35s recorded the reflectance value of about 0.172% with wavelength of 300nm. Sample C deposited at 40s recorded the lowest reflectance value of 0.14% with wavelength of 300nm. Since the transmittance of the ZnSe approximately remains constant at the visible and near infrared range, this makes ZnSe a good candidate to be used as antireflection coatings within this spectral range and useful in manufacturing optical components, windows, mirrors, lenses for high power infra red laser and others properties like solar cells fabrication.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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