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Structural Investigation of Zinc Selenide Thin Films

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Abstract: In the field of nanotechnologies nanoparticles are synthesized has made great strides and also in optoelectronics. Zinc Selenide (ZnSe) is a II-VI semiconductor with wide band gap and these semi conducting devices has wide range of applications in various optoelectronic devices and in solar cells. The high purity salt is taken for the deposition. The parameters like concentration [0.1 N], brushing time (50 min) and current (1 mA) are optimized to get polycrystalline films on the Fluorine doped Tin Oxide (FTO) Substrate. The X-Ray Diffraction (XRD) spectra are taken using PANalytical X'PERT-PRO powder X-ray diffractometer and the peaks are identified with the help of JCPDS values. For the as deposited ZnSe, many peaks are observed and in that one peak has (200) and (420) planes respectively for the presence of ZnSe and a broad peak is observed in 14.10° . X-ray diffraction measurement confirms the incorporation of ZnSe with a cubic structure and nanometer size. Photoluminescence spectrum of films is taken by Cary Eclipse EL08083851. The band in 484 nm (2.56 eV) is corresponds to the transition between the valence band to conduction band. The optical band gap value is comparable with Photoluminescence spectra.

Key words: ZnSe, X-ray diffraction, ultraviolet, optical properties

INTRODUCTION

Zinc Selenide (ZnSe) is an II-VI semiconductor with wide band gap and these semi conducting devices has wide range of applications in various optoelectronic devices and in solar cells. This type of Semiconductor has a direct band gap and in wide range of visible spectrum it is transparent. ZnSe thin films have Polycrystalline nature and these materials are used in electroluminescent display and window layers in solar cells. In recent years, considerable efforts have been denoted to develop blue green laser diodes based on ZnSe and its alloys so for these have not been realized, mainly because of the difficulty in controlling electrical conduction. Preparation of conductive layer is essential for its use light emitting devices of Zinc Selenide this films can be deposited by variety of methods like laser assisted evaporation (Aksas *et al.*, 2006), Atomic Layer Deposition (ALD) (Choudhury *et al.*, 2004), spin coating method (Guziewicz *et al.*, 2004). In this study, brush plating method was used to deposit zinc selenide thin films on FTO substrate, also seems to be a simple and inexpensive method for fabricating semiconductor films and the films were characterized for their structural and optical properties.

MATERIALS AND METHODS

All the parameters are optimized (deposition time 50 min, pH, concentration (1 N), deposition current (1 mA). Layers were brush plated on Fluorine doped Tin Oxide (FTO) coated conducting substrates. The negative terminal of power supply connected with a graphite rod wrapped in cotton wool served as the anode. The cotton wool behaves like a brushing tool. Prior to plating the stylus was wired to the power supply and the cotton wool was soaked in the electrolyte. The stylus was then made to contact with the FTO substrate and moved in one direction at uniform speed and repeat this step for 20 min. Whenever the stylus was contact with the substrate an electrical current was found to passing through the graphite. The electrolyte trapped within the cotton wool also associated with the acceleration of the ions which were subsequently forming the ZnSe layer on the substrate. The bath contained 1 g of Zinc Oxide and 0.05 g of Selenium di oxide (SeO₂). In each case, the power unit was preset at voltage value 1 V and the electrolyte temperature was at room temperature. The films were annealed in vacuum at 300 and 500°C for 2 h.

The structural investigations of zinc Selenide thin films were done by X-ray diffraction method. Structural

analysis using X'PERT-PRO diffractometer with CuK α radiation ($\lambda = 1.54060 \text{ \AA}$). A Hitachi UV-Vis-NIR spectrometer was used to carry out the optical studies. Photoluminescence measurements were carried out at room temperature by a method (Cary Eclipse Win FLR) with 600 nm.

RESULTS AND DISCUSSION

Structural Investigations: Figure 1 shows XRD patterns of the zinc selenide thin film as-deposited coated on FTO substrates. Well defined peaks are observed in the XRD patterns suggesting that the films are crystalline in nature. The observed peaks are compared with the standard JCPDS values show that the as-deposited on FTO substrate film gives a structure matching with (JCPDS 02-0479), zinc blend Cubic structure was obtained for as deposited ZnSe thin film with lattice parameter $a = 5.65 \text{ nm}$. The observed peak belong to ZnSe where detected at $2\theta = 14.3^\circ, 55.9^\circ, 37.9^\circ$ corresponding to interplanar distances of $6.5 \text{ \AA}, 2.5 \text{ \AA}, 2.4 \text{ \AA}$, respectively.

When the film is annealed up to 300°C we observed more randomized orientation of the crystallites than in the as prepared film. The structural composition does not change due to increased annealing temperatures up to 300°C . Figure 2 and 3 shows the XRD patterns of the film annealed in vacuum at 300 and 500°C for 2 h. The observed new peaks at $2\theta = 27.4^\circ, 37.9^\circ, 78.1^\circ$ corresponding to interplanar distances of $3.2 \text{ \AA}, 2.4 \text{ \AA}, 1.2 \text{ \AA}$ this pattern matches the standard pattern of stoichiometric ZnSe with $a = 3.996 \text{ nm}$ (JCPDS 15-0105). The intensity of the peaks was increased as the annealing temperature increased.

The crystallite grain size of the zinc selenide thin films was calculated using the Scherrer's formula:

$$D = 0.94\lambda/\beta\cos\theta \text{ (nm)}$$

The grain size increased from 6-31 nm as the annealing temperature increased. The strain and dislocation density were calculated using the following relations:.

$$\text{Strain } (\epsilon) = \beta\cos\theta/4$$

Where:

θ = Bragg angle

β = Full Width Half Maximum of the XRD peak (FWHM);

$$\text{Dislocation density } (\delta) = 15\epsilon/aD$$

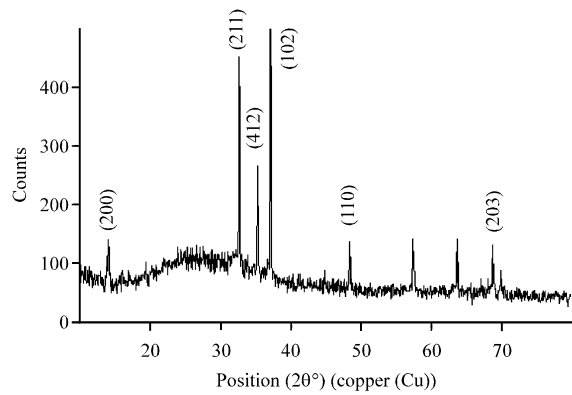


Fig. 1: XRD pattern of As-deposited film

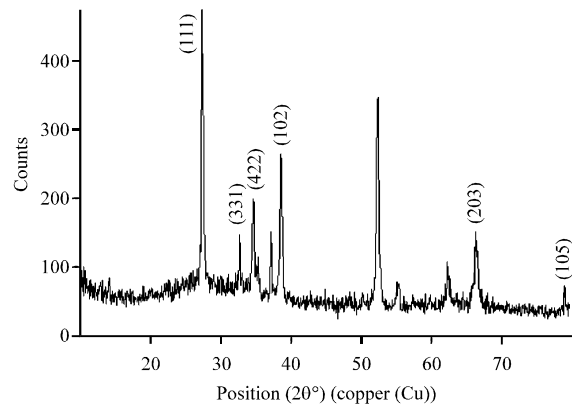


Fig. 2: XRD pattern of annealed film at 300°C

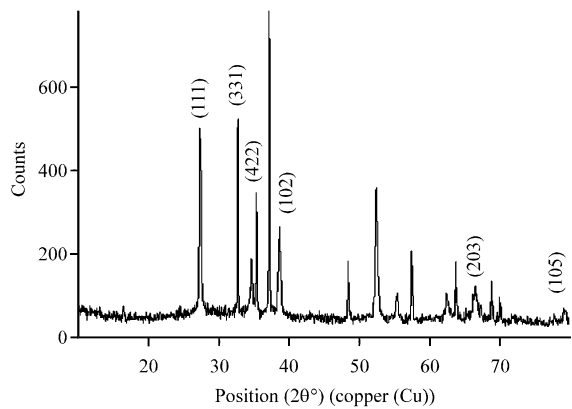


Fig. 3: XRD pattern of annealed film at 500°C

Where:

ϵ = Strain

a = Lattice parameter

D = Grain size

The value of strain increases from 2.48×10^{-2} - 3.60×10^{-2} as the annealing temperature increases. The

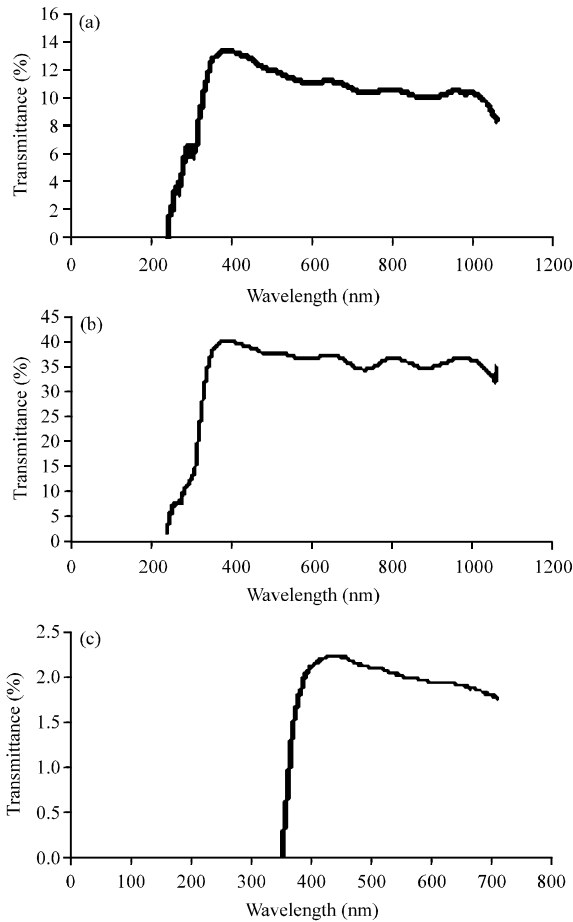


Fig. 4(a-c): Transmittance spectra for, (a) As-deposited (b) Annealed at 300°C and (c) Annealed at 500°C

observed dislocation density was increased from $0.017 \times 10^{14} \text{ m}^{-2}$ to $0.03 \times 10^{14} \text{ m}^{-2}$ (Choudhury *et al.*, 2004) reported the hkl indices of the film deposited by laser assisted evaporation had (111), (220), (311), (400) and (331) which has good agreement with the present study. Aksas *et al.* (2006) reported the presence of (111), (220), (311) with indices of the film deposited by spin coating method.

Optical studies: The optical absorbance and transmittance spectra of the films formed by brush plating method are shown in Fig. 4 and 5, respectively for the as-deposited and annealed (at 300 and 500°C) zinc selenide thin films. Annealing the film at 300 and 500°C produced some changes in the optical absorbance and transmittance spectra of the film. These changes are attributed to structural, compositional and crystalline process as discussed before.

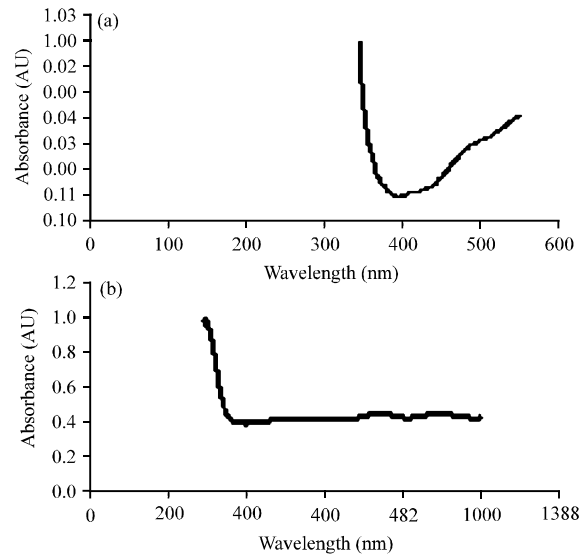


Fig. 5(a-b): Absorbance spectra for, (a) As-deposited and (b) Annealed at 300°C

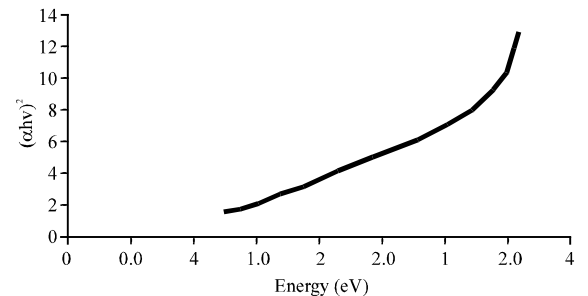


Fig. 6: Direct band gap of As-deposited film

The band gap values for the films were estimated from the absorption spectra. The corrected transmittance values are obtained by following expression:

$$T_{\text{corr}} = \frac{T(\%)}{100-R(\%)} \times 100$$

The transitions from the valance band to conduction band across the band gap at different wavelengths were calculated for obtaining the absorption coefficients (α_g):

$$\alpha_g = (1/t) \ln (100/T_{\text{corr}})$$

where, T_{corr} is the corrected transmittance values and t is the film thickness. The direct band gap value is obtained from following graph drawn between absorption coefficient α_g^2 against the corresponding values of photon energy ($h\nu$).

The energy gaps were determined from the Fig. 6 and 7. The as-deposited sample has a $E_{g\text{dir}}$ value of 2.75 eV and

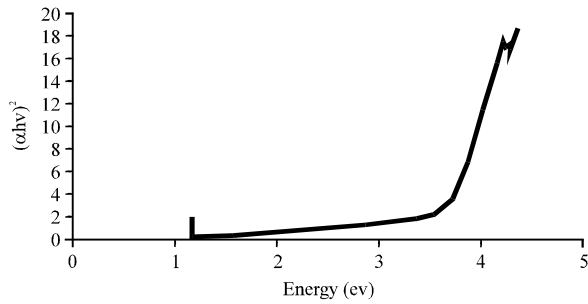


Fig. 7: Direct band gap of annealed film

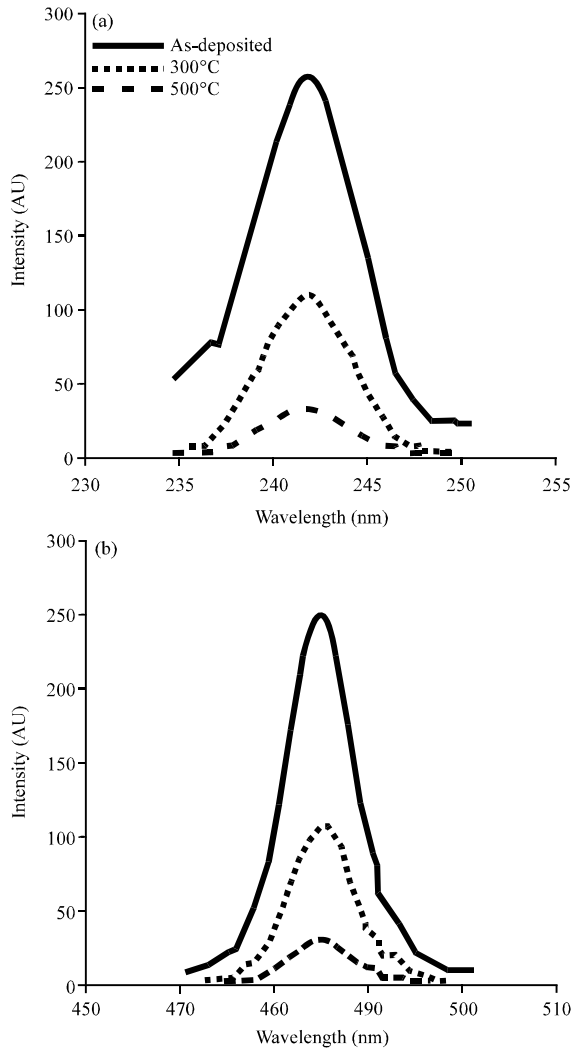


Fig. 8(a-b): Photoluminescence spectra for ZnSe thin films, (a) The photons are excited in the wavelength of 242 nm and (b) The emission of thin film is at the wavelength of 484 nm

for the annealed (300°C) has 3.38 eV. These band gap values are compared with earlier reported values. From this characterization these materials have good chance to be used for solar cells.

Photoluminescence: The photoluminescence spectra of ZnSe thin films are shown in Fig. 8. From the spectra, the photons are excited in the wavelength of 242 nm. The intensity of the peak Decreases as the annealing temperature increases. From the spectra the emission of ZnSe thin films is at the wavelength 484 nm. The optical band gap is comparable with Photoluminescence spectra.

CONCLUSION

Zinc selenide thin films were successfully deposited onto FTO substrates by brush plating technique. The films were uniform and had good adherence to the substrate. The XRD of zinc selenide films compared with Standard JCPDS (02-0479) and (15-0105). The average grain size of the films were determined and it increases from 6-35 nm as the annealing temperature increases. The energy gap values of the films were determined and compared with the reported one. The emitted and excited wavelength were determined from the photoluminescence spectra. The Zinc selenide films have wide applications in photovoltaic cells and solar conversion cells.

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