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Thickness Dependent Optical Properties of ZnSe Thin Films

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Abstract

Zinc Selenide (ZnSe) thin films of 100 – 500 nm thickness were deposited by electron beam evaporation technique and the optical properties were studied in correlation with film thickness. The 300 nm film exhibits 83% transmittance with very low absorption of optical energy in the visible region. The refractive index estimated by envelope technique was found to decrease with increase in thickness. The optical band gap for the deposited thin films were in the range of 2.79 – 2.40 eV. The surface topology indicates that the roughness was increased with increase in film thickness.

1. Introduction

Studies on II-VI semiconducting thin films have attracted several researchers for improving the efficiency of heterojunction solar cells. ZnSe, one of the promising semiconducting materials found to be one of the prominent candidates as an n-type buffer material in CdTe based solar cell due to its wide band gap of 2.67 eV [1]. ZnSe thin film has immense potential to use as an efficient window/buffer material when CdS thickness is relatively small (<100 nm) in CdS/CdTe solar cell due to its wide transmission range from 450 nm to 21.5 µm with high refractive index of 2.60 at 550 nm and high electrical resistivity (10^{12} Ωcm) [2, 3]. ZnSe thin films are also used as buffer layers for CIGS solar cells which reached the efficiency up to 9.6% (under AM 1.5 illumination) [4]. Many researchers have observed that by integrating different buffer layers in combination of zinc and tin oxide has improved the CdTe/CdS cell efficiency and reproducibility [5-7]. Due to these factors in the present investigation, the optical properties of e-beam evaporated ZnSe thin films of different thickness has been carried out and it was desired to identify the optically suitable thickness which can be used as a buffer layer for solar cells.

2. Experimental

The PVD apparatus we used is based on a commercial system developed by Hind High Vac. Co., Bangalore. The ZnSe powder source (99.99% purity, Sigma Aldrich, U.S.A) is brought into the chamber in a molybdenum crucible in vacuum condition at a pressure of 2 x 10^{-5} mbar. The soda lime glass slides of dimensions 25 mm × 15 mm × 1.35 mm were used as substrate. Glass substrates were degreased with soap water followed by ultra-sonication in double distilled water and ethanol. The substrate holder is aided with the continuous rotation for the formation of uniform films on the substrate surface. The films of different thickness from the range of 100 nm to 500 nm were deposited and the deposition rate was maintained constant at 5-8 A°/sec throughout the sample preparation. The thickness and deposition rate were measured using the quartz crystal thickness monitor (DTM-101). The deposited samples were annealed in air ambient at 100°C for 3 hrs.

The optical studies were performed using VIS-NIR spectrophotometer (Ocean Optics, USA. Model No. USB4000-XR). The optical constants like thickness and refractive index were estimated by using equations (1) and (2) by envelope technique [8].

$$t = \frac{\left(\lambda_{max} \times \lambda_{min}\right)}{4\left[n\left(\lambda_{max}\right)\lambda_{min} - n\left(\lambda_{min}\right)\lambda_{max}\right]} \quad (1)$$

$$\frac{1}{T_m} - \frac{1}{T_m} = \frac{1}{4}\frac{\left(n^2 - 1\right)\left(n^2 - n_s^2\right)}{n^2 n_s} \quad (2)$$

The absorption coefficient 'α' can be calculated using the relation [9],

$$\alpha = \left[\frac{2.303}{d}\right] \times \log\left(\frac{1}{T}\right) \quad (3)$$

The surface analysis of the prepared thin films was carried out using A100 Atomic Force Microscopy — A.P.E. Research (Italy).

3. Results and Discussion

The transmittance and reflectance spectra for ZnSe thin films deposited for different thickness (100 – 500 nm) is presented in figure 1. It is evident from the figure that, in the visible region, the films of lower thickness have a high transmission while the films of higher thickness exhibit low transmission. The maximum transmittance of 83% in visible region of the spectrum was observed for 300 nm film. The transmittance spectra exhibit wavy nature irrespective of the film thickness between the absorption edge to 800 nm. Similar trends of observations for the ZnSe films fabricated with substrate temperature have been reported elsewhere [9]. The spectra also reveal wide transmission range covering 400-800 nm for films having thickness greater than 200 nm.

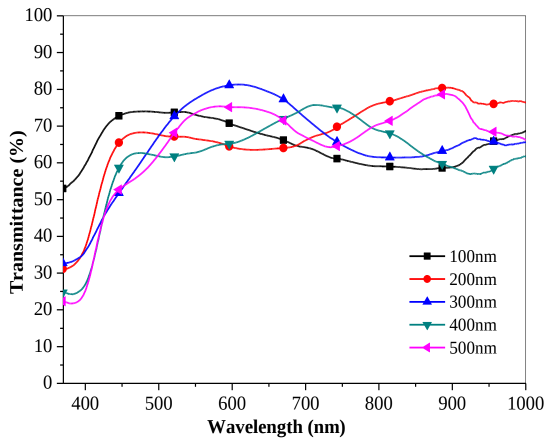

Figure 1. Transmittance spectra of ZnSe thin films of different thickness

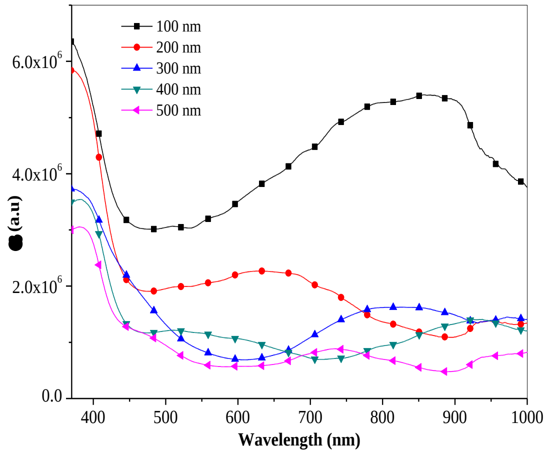

Figure 2. Absorption coefficient versus wavelength of ZnSe thin films

Figure 2 represents the optical absorption spectra of ZnSe films deposited onto a glass. The optical absorbance was calculated from transmittance spectra for the films of different thicknesses. The variation of optical absorbance with wavelength reveals a very low absorption of energy in the visible regions and high absorption in shorter wavelengths. The spectra also confirm that as the thickness of the film increases the absorption effect decreases at 550 nm this can be attributed to the transparency of the film at half wavelength thickness. This is also due to effect of index of refraction of the films.

The absorption coefficient can be written as a function of incident photon energy 'hν' [10],

$$\alpha h\nu = A_o\left(h\nu - E_g\right)^p \quad (4)$$

Where, E_g is the optical band gap, 'P' has discrete values like 1/2, 3/2, 2 or more depending on whether the transition is direct or indirect and allowed or forbidden. In the direct and allowed cases P=1/2 where as for the direct but forbidden cases it is 3/2. But for the indirect and allowed case P = 2 and for the forbidden cases it will be 3 or more. The value of 'P' determined the nature of optical transition. The results have been analysed according to the relation (4). A_o is a constant and given by

$$A_o = \left[{e^2}\big/{neh^2 m_e^*}\right]\left(2m_r\right)^{3/2} \quad (5)$$

Where, m_e^* and m_r are the effective and reduced masses of charges carriers respectively.

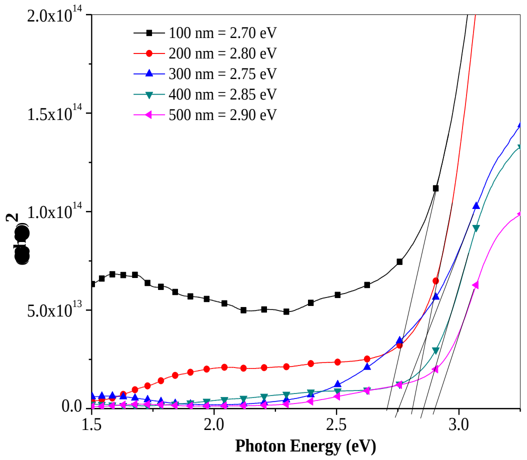

Figure 3. Band gap of ZnSe thin films of different thickness

Figure 3 shows the plot of $(\alpha h\nu)^2$ versus hν of ZnSe thin films. The 100 nm film has the direct band gap of 2.70 eV which is equal to the standard bulk band gap [11], the film also exhibits blue shift of 0.05 eV per 100 nm increase in thickness. The optical band-gap value for the deposited film for thickness from 100-500 nm is found to be increased in the range of 2.70 to 2.90 eV. The decrease in band-gap value may be attributed to the increase in particle size with decrease in refractive index. This thickness dependent optical band gap trend is because with increase in film thickness the free atoms will tend to create overlapping levels when individual atoms are brought closer to each other. Hence, as the film thickness increases there will be a several energy levels resulting in overlapping of energy bands of these films [12]. This phenomenon can be explained by Urbach tail which signifies the characteristic phenomena of absorption curve with respect to photon energy (Fig. 4).

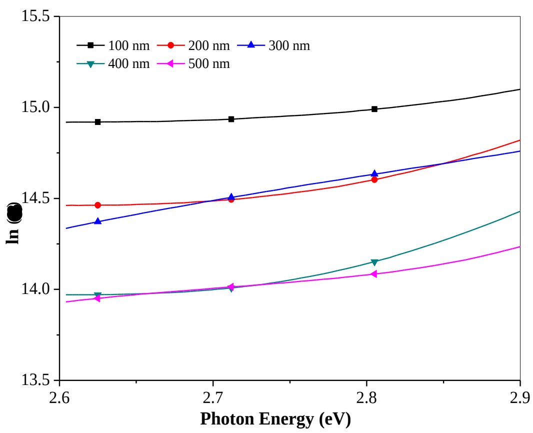

Figure 4. Variation of ln (α) versus photon energy of ZnSe thin films

If the structure of the film has disorderness, we can estimate the level of disorderness using this Urbach energy [13] which results in lean-in transmittance spectra towards minimum photon energy. The tail width of the films can be calculated by the slope of the straight line portion of the plot. The optical band gap (E_g) and the tail width (ΔE) of ZnSe thin films is shown in table 1.

Table 1. Variation of Band gap and tail width of ZnSe thin films

Thickness (nm)	100	200	300	400	500
Band Gap (eV)	2.70	2.80	2.75	2.85	2.90
Tail Width (eV)	0.89	1.71	1.41	2.1	1.37

The minimum tail width of 0.89 eV revealed by 100 nm thin film whereas 400 nm film exhibits higher tail width of 2.1 eV. The minimum tail width with better optical property depicted by 300 nm thin films indicates good crystallinity compared to rest of the thin films.

Figure 5 represents the value of Extinction Coefficient (k) versus wavelength. The Extinction coefficient is calculated using the equation,

$$k = \frac{2.303\lambda \log\left(\frac{1}{T_o}\right)}{4\pi d} \quad (6)$$

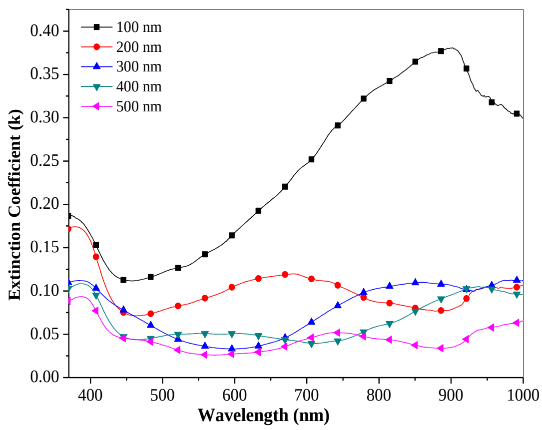

Figure 5. Variation of extinction coefficient versus wavelength of ZnSe thin films

The extinction coefficient is directly related to the absorption of light. In the case of polycrystalline films, extra absorption of light occurs at the grain boundaries [14]. This leads to non-zero value of (k) for photon energies smaller than the fundamental absorption edge [15]. This is further confirmed by figure 4.

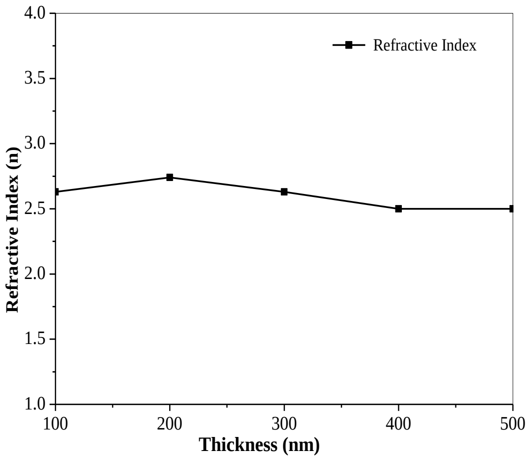

Figure 6. Variation of refractive index with thickness of ZnSe thin films

The refractive index 'n' of the deposited films is evaluated from envelope technique is shown in figure 6. The calculated values of refractive index corresponding to the thickness (200 – 500 nm) are found to be in the range of 2.74 to 2.50 respectively. All these values were considered at the half wavelength optical thickness of the thin films. Also, the high refractive index of these films at lower thickness makes it suitable for anti-reflective applications [16].

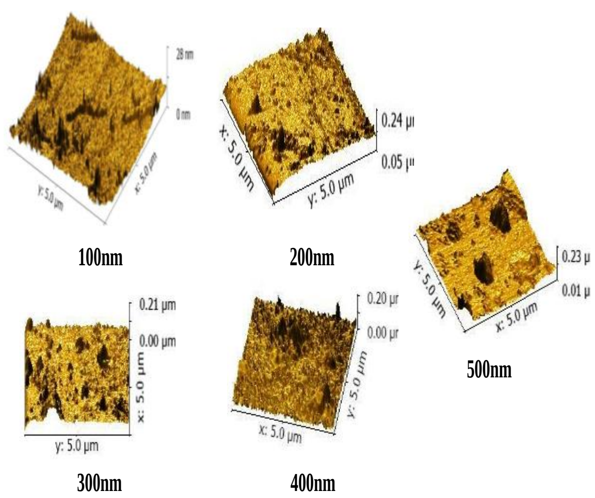

Figure 7. Surface morphology of ZnSe thin films

The topology of deposited ZnSe film surface is viewed three-dimensional AFM images is shown in Fig. 7. The AFM morphology clearly revealed that the deposition of ZnSe film took place with general thin film mechanism of nucleation growth. The ZnSe film was well uniform on the glass substrate without any cracks or pinholes. From the surface topology it confirms the presence of exaggerated bunch composed of nanoparticles. Further, AFM image clearly shows the three-dimensional growth of ZnSe thin film with more surface roughness with increase in thickness which can be attributed due to the defects of the films at higher film thickness. The defects can be overcome by densification of the films annealing for higher temperatures there by reducing the defects. The calculated rms roughness and average roughness values are given in Table 2.

Table 2. RMS roughness of ZnSe thin films deposited for different thickness.

Thickness (nm)	Surface Roughness (SA)	
	RMS Roughness (nm)	Average Roughness (nm)
100	2.47	2.19
200	13.1	9.0
300	17.8	10.7
400	22.6	15.6
500	28.1	18.8

4. Conclusions

The detailed investigations on optical properties of ZnSe thin films of 100 - 500 nm thickness was carried out in the Visible – Near Infrared regions. The transition of the deposited film is direct, and the optical band gap values increased (2.70- 2.90 eV) with the increase in film thickness. The films exhibit decrease in refractive index (2.74 - 2.50) with increase in thickness. The surface morphology indicates that rms value increases with increase in film thickness. The 300 nm thin film has peak transmittance of 83% at 600 nm with low rate of absorption and appropriate band gap having average surface roughness of 10.6 nm makes the film can be used as window material for solar photovoltaic's and optoelectronic device applications.

5. Acknowledgement

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