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Effect of Thermal Annealing on the Band GAP and Optical Properties of Chemical Bath Deposited ZnSe Thin Films

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Abstract

Zinc selenide (ZnSe) thin films were deposited on glass substrate using the chemical bath deposition method at room temperature from aqueous solutions of zinc sulphate and sodium selenosulfate in which sodium hydroxide was employed as complexing agents. The 'as-deposited' ZnSe thin films are red in color and annealed in oven at 473 K for 1 hour and on a hot plate in open air at 333 K for 5 minutes, affecting the morphological and optical properties. Optical properties such as absorption coefficient α and extinction coefficient k, were determined using the absorbance and transmission measurement from Unico UV-2102 PC spectrophotometer, at normal incidence of light in the wavelength range of 200–1000 nm. The films have transmittance in VIS-NIR regions that range between 26 and 87%. From absorbance and transmittance spectra, the band gap energy determined ranged between 1.60 eV and 1.75 for the 'as deposited' samples, and the annealed samples exhibited a band gap shift of 0.15 eV. The high transmittance of the films together with its large band gap made them good materials for selective coatings for solar cells.

Key Words: Chemical bath Deposition, ZnSe Thin film, band gap, Solar Cells.

1. Introduction

Binary compounds of group IIB and group VIA elements are commonly referred to as II-VI compounds. They have important technological applications and among these, the only compounds that can be prepared in both n- and p-type forms are cadmium telluride (CdTe) and zinc selenide (ZnSe). Preparations of thin films of these compounds are most often done via vacuum evaporation, chemical vapor deposition, sputtering and spray pyrolysis method. The deposition of ZnSe thin films have also been carried out by molecular beam epitaxy and chemical vapor deposition. There are several reports on the electrodeposition of ZnSe thin films from aqueous solutions as well as from molten salts [1–2]. However, little study has been reported about the chemical bath deposited (CBD) ZnSe thin films [3–5]. For the films deposited and characterized using XPS it observed they are composed of a mixture of ZnSe and ZnO (or $Zn(OH)_2$, for non-annealed films). It was also observed that the films are richer in ZnO, being close to the film/substrate interface, with increasing ZnSe

proportion above [4]. CBD is widely used for the large-scale production of films owing to its low production cost and simplicity of operation.

Depending on the CDB conditions, the films present either a gray or red coloration depending on whether they have an excess of Zn or Se, respectively.

In this paper, deposition of ZnSe thin films by CBD method at room temperature on glass substrates and the effect of annealing at various temperatures on the band gap are presented.

The effect of annealing of ZnSe thin films on band gap was studied by optical absorption and transmission.

2. Experimental Method

Zinc selenide thin films were deposited on glass substrates using the CBD method. The reagents used were zinc sulphate, selenium, sodium hydroxide and sodium sulphate. Sodium selenosulphate was obtained by dissolving 8 g selenium powder mixed with 24 g sodium sulphate in 100 ml of water and heating to 80 °C.

To obtain the deposition of thin films, 5 ml of 1 M zinc sulphate was placed in a 50 ml glass beaker and 4.8 ml NaOH was slowly added to it with constant stirring. The solution initially was milky and turbid due to the formation of a $Zn(OH)_2$ suspension. Addition of excess NaOH led to the dissolution of the turbidity and made the solution clear and transparent, and also reduced Zn^{2+} in concentration. 2 ml of freshly prepared 1 M Na_2SeSO_3 was slowly added to this, with constant stirring. The chemical bath was made up to 50 ml with distilled water. The pH of the final reaction mixture was $\sim 11 \pm 1$. The solution was stirred for a few seconds and a cleaned glass substrate which was previous degreased in HCl for 48 hours, rinsed in distilled water and dried in air, inserted vertically into the chemical bath solution and maintained at room temperature ($\sim$300 K). The substrate coated with ZnSe thin films was removed at suitable intervals after about 2.5 hrs, rinsed with distilled water, and dried in air. Films prepared by this method were uniform, well adherent to the substrates and red in color.

Deposition of ZnSe thin films occurs when the ionic product of Zn^{2+} and Se^{2-} ions exceeds the solubility product of ZnSe. The control of Zn^{2+} and Se^{2-} ions in the solution controls the rate of precipitation and hence the rate of film formation. The steps involved in the chemical deposition of ZnSe thin film are given below.

The hydrolyses of sodium selenosulphate (Na_2SeSO_3) in solution to give Se^{2-} ions proceeds via the chemical reactions

$Na_2SeSO_3 + OH^+ \leftrightarrow Na_2SO_4 + HSe^-$

$HSe^- + OH^- \leftrightarrow H_2O + Se^{2-}$.

The reaction process between Zn^{2+} and NaOH proceeds via

$ZnSO_4 + 2NaOH \leftrightarrow Zn(OH)_2 + Na_2SO_4$.

When the NaOH is added to the Zn^{2+} salt solution, $Zn(OH)_2$ starts precipitating when the solubility product (SP) of $Zn(OH)_2$ is exceeded, i.e.

$Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)_2$.

The $Zn(OH)_2$ precipitate dissolves in excess NaOH solution to form the complex sodium zinc hydroxides $Na_4Zn(OH)_6$

$Zn^{2+} + 4NaOH \leftrightarrow Na_4Zn(OH)_6$

$Na_4Zn(OH)_2 \leftrightarrow 4Na^+ + HZnO_2^- + 3OH^- + H_2O$.

Finally, ZnSe thin film formation takes place via

$HZnO_2^- + HSe^- \leftrightarrow ZnSe + 2OH^-$.

The growth mechanism of thin films from CBD involves a nucleation phase in which an initial layer of $Zn(OH)_2$ formed on the glass substrate is chemically converted into ZnSe by the reaction with Se^{2-} ions available in the bath by the hydrolysis of selenosulphate.

In this study ZnSe films have been deposited at a very low temperature (300 K). Due to the low deposition temperature and slow rate of deposition, growth processes are based on the slow release of Zn^{2+} and Se^{2-}

ions in the solution, which then condense on an ion-by-ion basis on the substrates, which are vertically mounted in the solution.

In order to get good quality ZnSe films, the preparation parameters involving zinc concentration, deposition time and pH were optimized. To study the effect of air annealing on the various film properties, films were annealed in open air using a hot plate at 453 K for 5minutes, then in oven at 423 K for 1 hour.

The as-deposited and annealed ZnSe film was characterized using a Unico UV-2102 PC spectrophotometer, a Philips PW1800 diffractometer and an optical microscope.

3. Results and Analysis

In order to study the crystalline nature of the thin films, the XRD patterns were studied. The thin films were scanned continuously between 0 to 70 at a step size of 0.03 and at time per step of 0.15 s. Figure 1 shows intensity of peak versus diffraction angle 2θ for a thin film using CuK_α radiation source with wavelength 1.54056 Å.

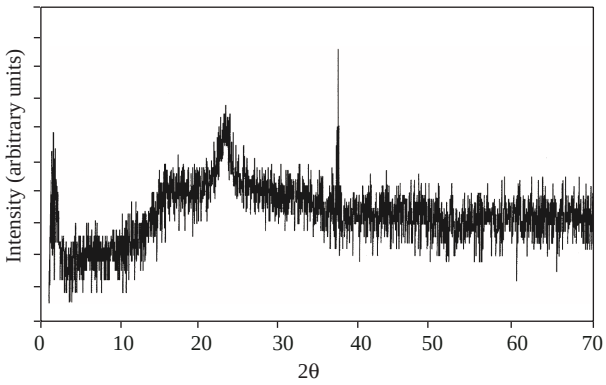

Figure 1. XRD result for ZnSe thin film.

The observed XRD peaks are at 15.065°, 22.840°, 37.025°, 51.470° and 68.540° with d-values 5.876, 3.890, 2.426, 1.774, and 1.368, respectively. The 37.025° fairly agrees with the preferred orientation along the (200) plane reported by Oztas et al. [2] while peaks at 22.025°, 51.470° and 68.540° agree fairly with the preferred orientation along the (111), (311) and (400) planes, respectively, as reported by Karanikolos et al. [1].

Optical measurements on the ZnSe thin films were performed on a Unico UV-2102 PC spectrophotometer. During scanning, a blank glass slide was placed in one of the beam's direction and another glass slide with film deposit was in the other beam's direction. Thus, the absorption spectrum displayed by the Unico UV-2102 PC spectrophotometer was a result of the film deposited on the glass slide.

The optical absorption spectra of ZnSe films deposited onto a glass substrate were studied at room temperature in the range of wavelengths 200–998 nm. The variation of absorbance A and transmission T with wavelength λ are shown Figures 2 and 3, respectively.

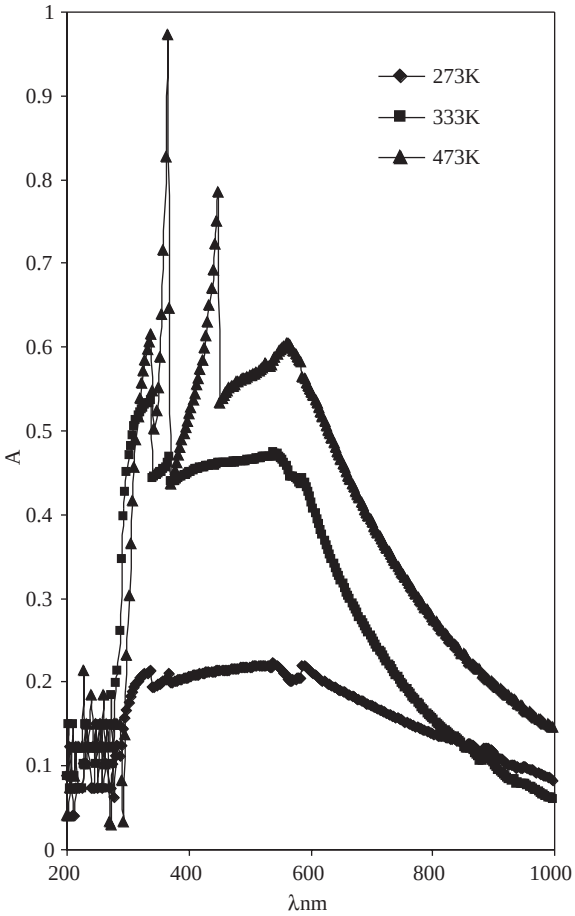

Figure 2. Plots of absorbance A against wavelength λ for ZnSe thin films at various temperatures.

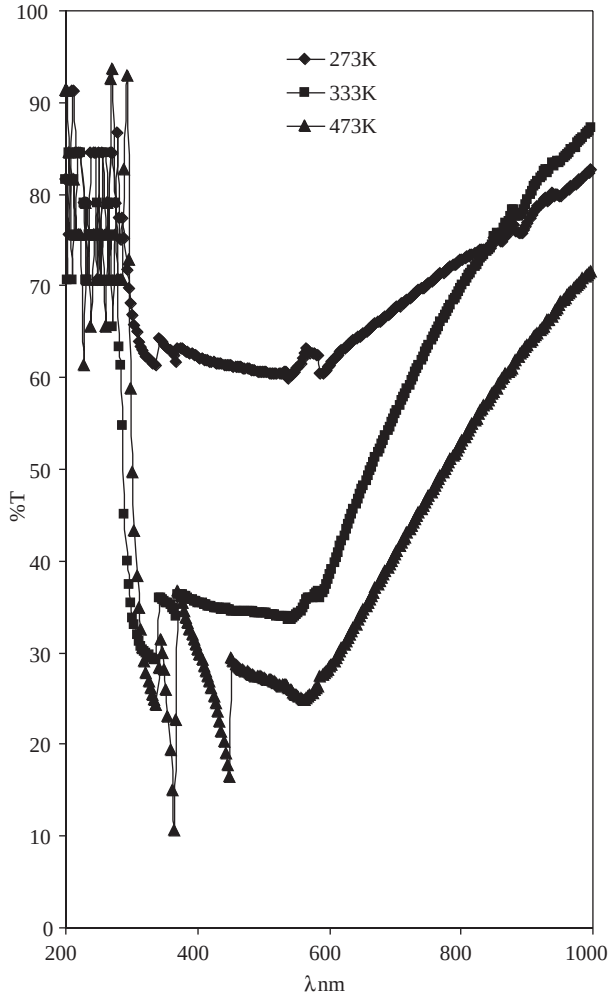

Figure 3. Plots of transmittance T against wavelength λ for ZnSe thin films at various temperatures.

The details of the mathematical determination of the absorption coefficient can be found in literature [6–9] while the plots absorption coefficient against photon energy is shown in Figure 4.

These absorption spectra, which are the most direct and perhaps simplest method for probing the band structure of semiconductors, are employed in the determination of the energy gap, E_g. The films show an increase in absorbance and a decrease in transmission after annealing the film at 333 K and 473 K in hot plate and oven, respectively. This is possibly due to the increase in grain size, the decrease in the number of defects and the change in color from red to black. E_g was calculated using the following relation [6–10]:

$$\alpha = A(h\nu - E_g)^n/h\nu,$$

where A is a constant and n is a constant, equal to 1/2 for direct band gap semiconductors. The estimated band gaps from the plots of $(\alpha h\nu)^2$ versus hν are shown in Figure 5, for as-deposited and annealed ZnSe films. The linear nature of the plot indicates the existence of the direct transition.

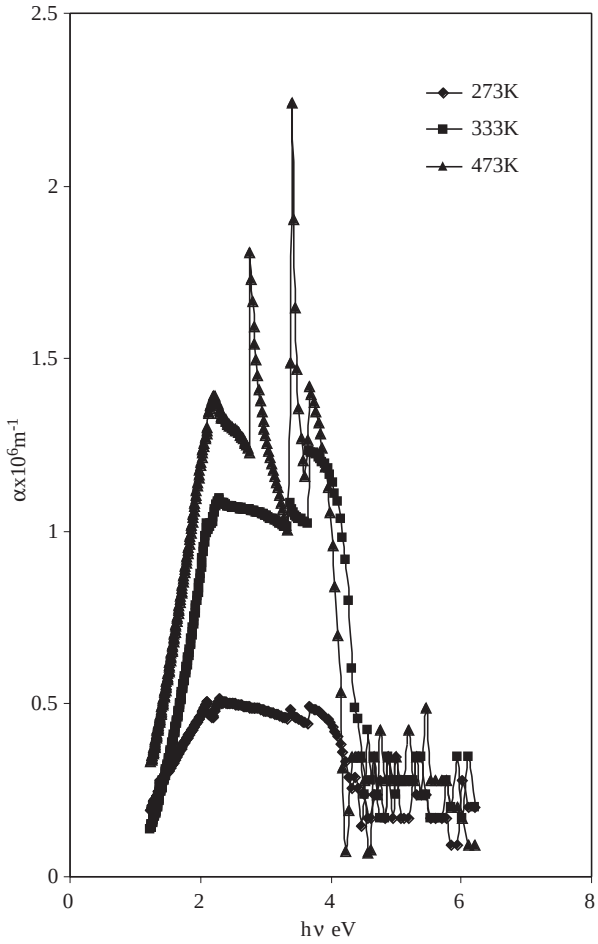

Figure 4. Plots of absorption coefficient a against Photon Energy hν for ZnSe thin films at various temperatures.

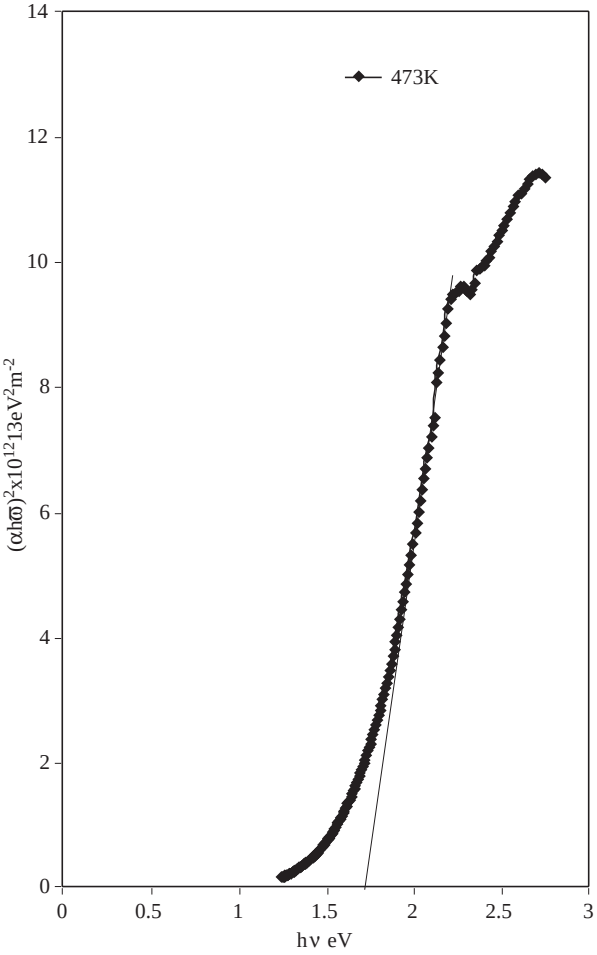

Figure 5. Plots of $(ah\nu)^2$ against photon energy hν for ZnSe thin film at 473 K.

The band gap E_g was determined by extrapolating the straight portion to the energy axis at $\alpha = 0$. It was found to be 1.60 eV for as-deposited ZnSe films and shows 1.10 blueshift from the normal bulk value (2.70 eV) [2]. This may be due to the deposition condition employed and the nature of ZnSe thin film, which results in a decrease in band gap. A band gap shift has been reported in some other compounds [11] using chemical bath deposition method. The band gap of the annealed ZnSe thin films were found to be 1.70 eV and 1.75 eV, which shows 1.00 eV and 0.95 eV blueshifts from the normal bulk value. The increase in band gap from 1.60 eV to 1.70 eV and 1.75 eV shows that annealing the film causes a strong redshifts of 0.10 eV and 0.15 eV in the optical spectra to that of characteristic bulk ZnSe. These changes have been attributed to the morphological dependent properties of the energy band gap. Estrada et al. [3] reported that ZnSe films possess optical bandgap nearly equal to 2.63 eV while the as-deposited ZnSe films are reported by Lokhade et al. [5] to be amorphous, Zn rich with optical band gap equal to 2.9 eV. Ortas et al. [2] reported values that range between 2.63 and 2.71 eV for both as-deposited and annealed thin films. The reason for variations with other reported values are attributed to the morphological nature and deposition conditions for the films.

The photomicrographs of the films viewed with an optical microscope (×100) are shown in Figure 6.

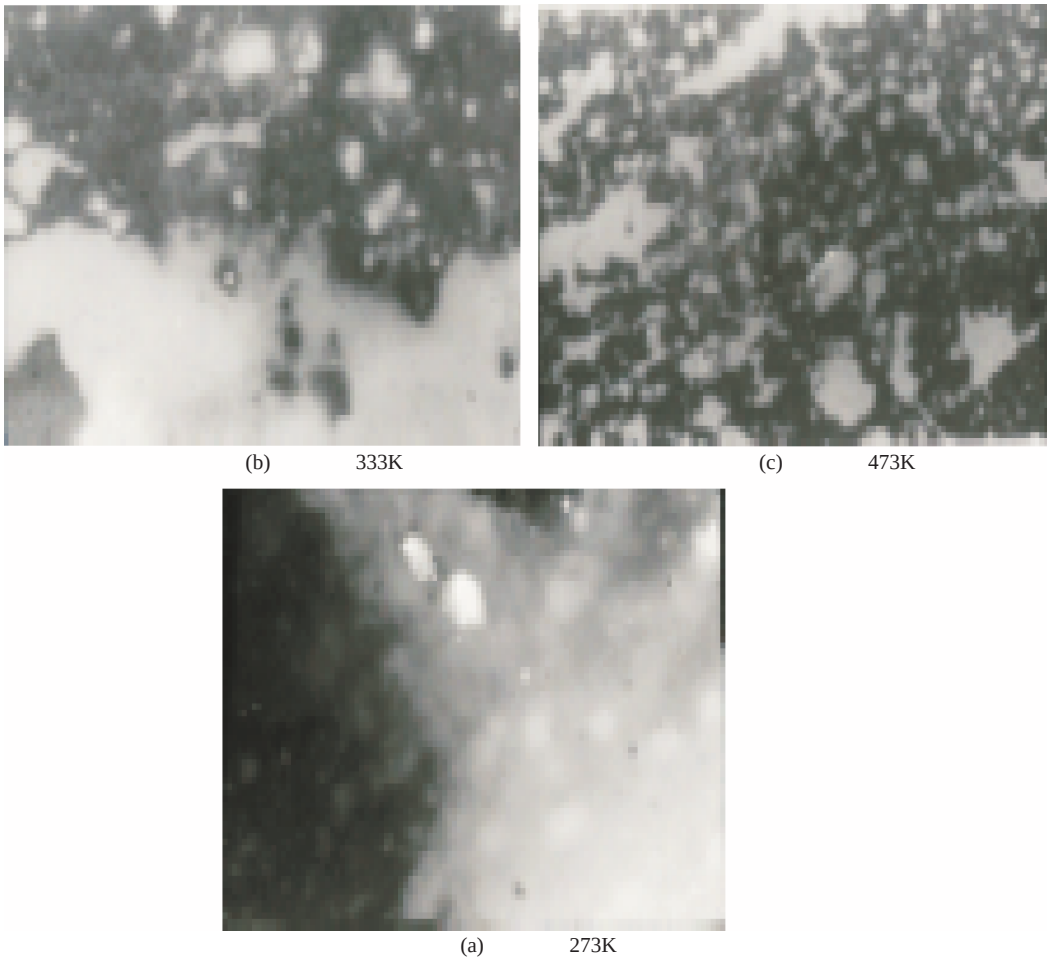

Figure 6. Optical micrographs of (a) as deposited ZnSe thin film (at 273 K) and annealed (b) at 333 K and (c) at 473 K.

It was observed that the different structures of the films confirmed the reasons for the band gap shifts. The films initially show absorbance in the ultraviolet but increased as wavelength approaches the VIS region (0.35 μm–0.40 μm); the films also showed high absorbance in the visible (0.39 μm–0.77 μm) but started decreasing towards the near infrared (0.70 μm–0.998 μm) of the electromagnetic spectrum and showed low energy gaps. Hence, they could serve as potential solar cells material with other suitable thin film materials for photovoltaic generation of electricity. Since ZnSe is normally n-type [2], the growth of sufficiently low resistivity p-type layers on ZnSe substrates is sufficient to produce high performance ZnSe $p-n$ junction, which is directly formed on the high quality n-type ZnSe substrates, which is requirement for solar cell fabrications.

4. Conclusion

ZnSe thin films deposited by an aqueous alkaline medium at room temperature show band gap 1.60 eV which under annealing on hot plate was found to be 1.70 eV, and 1.80 eV in an oven. Under air annealing, the film shows a redshift of 0.10 eV and 0.20 eV in its optical spectra. Such dependence has been attributed to the morphological nature of the film in chemically deposited thin films as seen under optical microscope.

The films initially show absorbance in the ultraviolet but increased as it approaches the VIS region (0.35 μm–0.40 μm), it showed high absorbance in the visible (0.39 μm–0.77 μm) but started decreasing towards the near infrared (0.70 μm–0.998 μm) of the electromagnetic spectrum and showed low energy gaps. Hence, they could be used as solar cells with other suitable thin film materials for photovoltaic generation of electricity.

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