Chalcogenide Letters Vol. 4, No. 6, June 2007, p. 69 - 75

BAND GAP SHIFT AND OPTICAL CHARACTERIZATION OF CHEMICAL BATH DEPOSITED CdSSe THIN FILMS ON ANNEALING

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Cadmium selenide (CdSSe) thin films were deposited on glass substrate using the chemical bath deposition method at room temperature from aqueous solutions of cadmium chloride ($CdCl_2.2½H_2O$) and sodium selenosulphate in which ammonium solution was employed as complexing agents. The 'as-deposited' CdSSe thin films are red in colour and specularly reflective. The 'as-deposited' film is annealed in air at 423K for 5minutes in a hot plate which affected the morphological and optical properties. The optical properties such as absorption coefficient (α was 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 average transmittance of the film in VIS-NIR regions ranges between 66 and 82%. From absorbance and transmittance spectra, the band gap energy determined is 3.22 eV for the 'as deposited' and 2.68 eV for the annealed which gave a band gap shift of 0.54 eV. The high transmittance of the films together with its large band gap made them good materials for selective coatings for solar cells.

(Received March 14, 2007; accepted June 20, 2007)

Keywords: CdSSe, Thin film, Band gap shift, CVD

1. Introduction

Micro crystallites of the mixed semiconductor CdSSe are of practical interest due to their optical and mechanical properties [1,2]. They are used as filters [3,4], optical waveguides [5] holography [6] and temperature sensor [7].

Thin films of CdSSe solid solutions have been deposited onto glass substrates by thermal evaporation of the bulk material in vacuum [8], by laser evaporation deposition on quartz [9], by novel wet chemical route on ITO-coated glass substrates [10]. Ternary alloy CdSSe nanowires and nanoribbons were successfully grown through a one-step thermal evaporation route using Au as a catalyst [11]. Thin films of cadmium sulphoselenide (CdSSe) have been chemically deposited using cadmium salt, thiourea and sodium selenosulphate [12]. The optical absorption studies showed that as Se content in CdS film increases, bandgap, E_g decreases from 2.5 eV (CdS) to 1.8 eV (CdSe) [12]. Among these various other techniques, the chemical bath deposition (CBD) method is found to be a cheap and simple way to deposit large area metal chalcogenide thin films [13-21]. Different preparation parameters such as the sources of metal ions, concentration of metal ions, sources of chalcogenide ions, concentration of chalcogenide ions, the pH of the resultant solution, deposition time, temperature etc and also heat treatments, like annealing in air, open air in hot plate, vacuum or different gaseous environments affect the properties of materials prepared by the CBD method. The paper describes the deposition of CdSe film using the CBD method and its modification after open air annealing in hot plate.

2. Experimental method

Cadmium sulphoselenide thin films were deposited on glass substrates using the CBD method. The reagents used were cadmium chloride, selenium, ammonia and sodium sulphate. Sodium selenosulphate was obtained by dissolving 8 g selenium powder mixed 24g sodium sulphate in 100ml of water and heating to 80 ^oC.

To obtain the deposition of thin films, 2 ml of 1M cadmium chloride was taken in a 100ml glass beaker and 1ml 100% ammonia was slowly added to it with constant stirring. The solution initially was milky and turbid due to the formation of a $Cd(OH)_2$ suspension. On addition of excess

ammonia led to the dissolving of the turbidity and made the solution clear and transparent, and also reduced Cd^{2+} in concentration. 10 ml of freshly prepared 1 M Na_2SeSO_3 was added slowly to this, and with constant stirring. The chemical bath was made up to 80ml with distilled water. The pH of the final reaction mixture was ~11 ± 1. The solution was stirred for a few seconds and a cleaned glass substrate which was previous degreased in HCl for 48hours, rinsed in distilled and dried air inserted vertically into the chemical bath solution and maintained at room temperature (300 K). The substrate coated with CdSSe thin films was removed at suitable intervals (5-10hrs), rinsed with distilled water, and dried in air. Films prepared by this method were uniform, well adherent to the substrates and red in colour.

The CdSSe films are deposited from ammonia solutions using sodium selenosulphate as a source of S^{2-} and Se^{2-} ions and cadmium–ammonia complex ions as cadmium precursors. The deposition of CdSSe thin films occurs; when the ionic product of Cd^{2+} and Se^{2-} or Cd^{2+} and S^{2-} ions exceeds the solubility product of CdSe or CdS. The control of Cd^{2+} and Se^{2-} or Cd^{2+} and S^{2-} ions in the solution controls the rate of precipitation and hence the rate of film formation [20]. This was achieved by using a stable complex for Cd^{2+} ions and a proper selenium ion source.

The steps involved in the chemical deposition of CdSe thin film are given below.

The hydrolyses of sodium selenosulphate (Na_2SeSO_3) in solution to give Se^{2-} ions is according to the chemical reaction

$$\begin{aligned} Na_2SeSO_3 + OH^- &\leftrightarrow Na_2SO_4 + HSe^- \\ Na_2SeSO_3 + OH^- &\leftrightarrow Na_2SeO_4 + HS^- \\ HSe^- + OH^- &\leftrightarrow H_2O + Se^{2-} \\ HS^- + OH^- &\leftrightarrow H_2O + S^{2-} \end{aligned} \quad (1)$$

Similarly, the hydrolyses of ammonia in water to give OH^- ions is according to the equation,

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (2)$$

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

$$Cd^{2+} + 2OH^- \leftrightarrow Cd(OH)_2 \quad (3)$$

The $Cd(OH)_2$ precipitate dissolves in excess ammonia solution to form the complex cadmium tetra-amine ions $[Cd(NH_3)_4]^{2+}$

$$Cd^{2+} + 4NH_3 \leftrightarrow [CdNH_3)_4]^{2+} \quad (4)$$

Finally, the CdSSe thin film formation takes place,

$$[CdNH_3)_4]^{2+} + Se^{2-} + S^{2-} \leftrightarrow CdSSe + 4NH_3 \quad (5)$$

The growth mechanism of thin films using the CBD method can take place either in the bulk of the solution (homogeneous precipitation process) or at the substrate surface (heterogeneous process). It can be considered as a ‘cluster by cluster’ growth, leading to particulate films. The latter is a growth mechanism involving the reaction of atomic species at the surface; it corresponds to an atom by atom process, also called an ‘ion by ion’ process [22].

In this study CdSSe 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 Cd^{2+} and Se^{2-} or Cd^{2+} and S^{2-} ions in the solution, which then condense with an ‘ion by ion’ basis on the substrates that are vertically mounted in the solution.

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

The ‘as-deposited’ and annealed CdSSe film was characterized by using Unico UV-2102 PC spectrophotometer.

3. Results and analysis

The XRD patterns of the crystal nature of the thin films were studied using CuKα radiation source with wavelength 1.54056Å. The scanning were done continuously between 0^o and 70^o at a step size of 0.03 and at time per step of 0.15s on $CdS_{10-x}Se_x$ thin films deposited onto glass at substrate temperatures 300K and annealed to various temperatures is shown in Fig. 1. A close look at this figure reveals that the diffraction pattern peaks that appeared at $2\theta = 37.04^o$ and 43.25^o. The XRD peaks exhibited by the heated films match the standard pattern of $Cd_{10}S_{5.71}Se_{4.29}$ (PDF#40-0838).

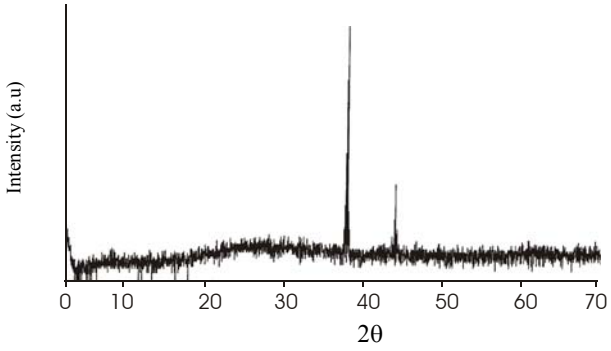

Fig. 1. XRD Pattern for $Cd_{10}S_{5.71}Se_{4.29}$.

Optical measurements on the CdSSe 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 as a result of the film deposited on the glass slide.

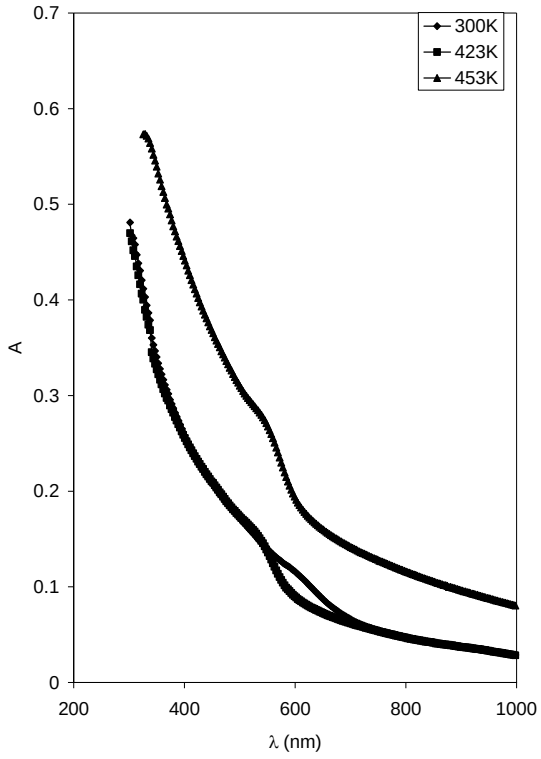

Fig. 2. Absorbance (A) as a function of wavelength (λ) for CdSSe thin film.

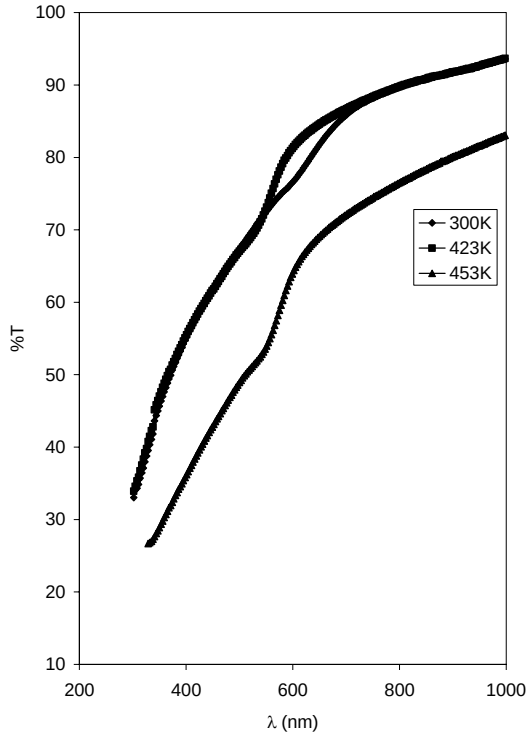

Fig. 3. Transmitance (T) as a function of wavelength (λ) for CdSSe thin film.

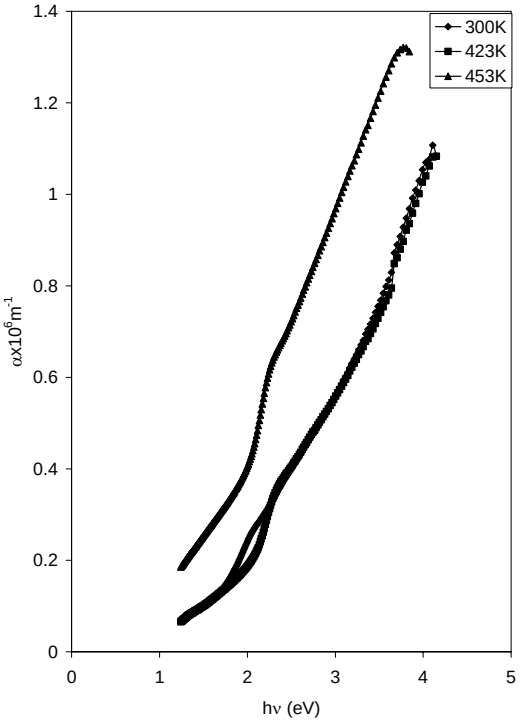

Fig. 4. Plots of absorption coefficient (α) as a function of photon energy (hν) for CdSSe thin film.

The optical absorption spectra of CdSSe films deposited onto a glass substrate were studied at room temperature in the range of wavelengths 200– 998nm. The variation of absorbance (A) and

transmission (%T) with wavelength (λ) are shown Figs. 2 and 3 respectively. The details of the mathematical determination of the absorption coefficient could be found in literature [13,17,18,23], while the plots absorption coefficient against photon energy is shown in Fig. 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 453K in hot plate. This is possibly due to the increase in grain size, the decrease in the number of defects and the change in colour from red to black. It is clearly seen from the optical spectra that the absorption and transmission edge shifts towards a longer wavelength for the film annealed at 453K. This shift indicates a decrease of the optical band gap 'E_g'. 'E_g' was calculated using the following relation [16, 17, 24]:

$$\alpha = A(h\nu - E_g)^n / h\nu \quad (6)$$

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 Fig. 5, for 'as-deposited' and annealed CdSSe films. The linear nature of the plot indicates the existence of the direct transition.

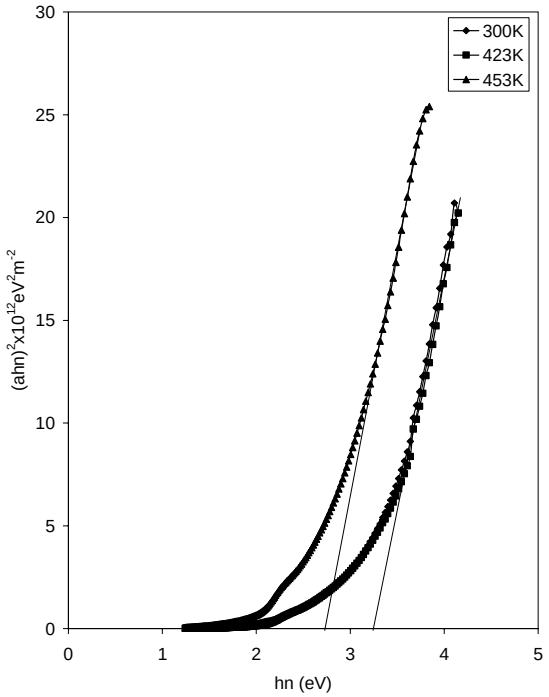

Fig. 5. Plots of $(\alpha h\nu)^2$ as a function of photon energy (hν) for CdSSe thin film.

The band gap 'E_g' was determined by extrapolating the straight portion to the energy axis at α =0. It was found to be 3.22 eV for as-deposited CdSSe films. This is close to reported value (2.00-3.00 eV) [2]. The band gap of the annealed CdSSe thin film was found to be 2.68 eV. This annealed bandgap is close to that reported value between 1.80 and 2.50 eV [12]. The reason for variations with other reported values are attributed to the crystal nature and deposition conditions for the films.

The decrease in band gap from 3.22 eV to 2.68 eV shows that annealing the film causes a strong 'redshift' of 0.54 eV in the optical spectra. These changes have been attributed to the crystallite size-dependent properties of the energy band gap. Similar 'redshift' in band gap energy 'E_g' values for the films with smaller thickness and/ or crystallite sizes have been reported for chemically deposited CdSSe thin films [21].

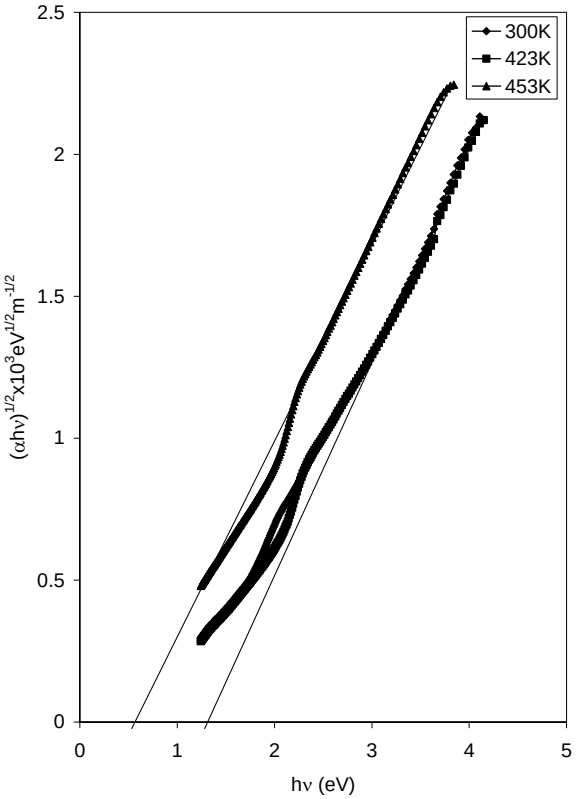

Fig. 6. Plots of $(\alpha h\nu)^{1/2}$ as a function of photon energy (hν) for CdSSe thin film.

A plots of $(\alpha h\nu)^{1/2}$ against hν for CdSSe films are shown in Fig. 6.These reveal band gaps between 0.60 eV and 1.30 eV.

The photomicrographs of the films viewed with an optical microscope (X 100) are shown in Fig. 7. It was observed that the structures of the films were crystalline and confirmed the reasons for the band gap shifts. The annealing of the film can be seen to have improved the crystal nature of the film and eliminated the incorporated selenium.

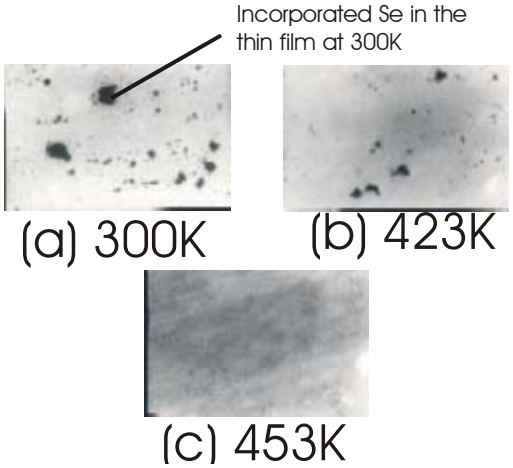

Fig. 7. Optical micrograph CdSSe thin films (X100)

The films have high absorbance in the ultraviolet (0.35 µm-0.40 µm), in the visible (0.39 µm-0.77µm) and in the near infrared (0.70 µm-0.998 µm) of the electromagnetic spectrum and also wide

energy gaps. Hence, they could be used to form p-n junction solar cells with other suitable thin film materials for photovoltaic generation of electricity and as well could serve as good window layers for photocells.

4. Conclusion

CdSSe thin films deposited by an aqueous alkaline medium at room temperature show band gap 3.22 eV which under annealing in hot plate was found to be 2.68 eV improved the crystallinity of films. Due to air annealing, the film shows a 'redshift' of 0.6 eV in its optical spectra. Such dependence has been attributed to the crystallite size effect in chemically deposited thin films as seen under optical microscope. The films have high absorbance in the ultraviolet (0.35 μm-0.40 μm), in the visible (0.39 μm-0.77 μm) and in the near infrared (0.70 μm-0.998 μm) of the electromagnetic spectrum and wide energy gaps. Hence, they could be used to form p-n junction solar cells with other suitable thin film materials for photovoltaic generation of electricity and serve as good window layers for photocells.

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