J. Nepal Chem. Soc., vol. 30, 2012

Liquid Phase Chemical Deposition of High Tech ZnSe Thin Flims

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Abstract

Being a promising and potential candidate for optoelectronic device applications, zinc selenide thin films were obtained for the first time on the glass microslides using a liquid phase chemical bath deposition. The deposition conditions, such as bath temperature (70 ^{0}C), deposition time (210 mins.), reaction pH (10.5± 0.2) and quantity of hydrazine hydrate (reducing agent) were finalized and the possible growth mechanism and reaction kinetics have been suggested. As the ZnSe films grow well in strong reducing atmosphere, the quantity of hydrazine hydrate was varied from 2 ml to 15 ml and ZnSe samples were obtained. The final product ZnSe thin films are physically hard, tightly adherent, relatively uniform and diffusely reflecting with light brown colored tinge in smoky appearance. An EDS analysis showed that the film stoichiometry depends on quantity of the added reducing agent in the bath. Structural studies were carried out on these films by an X-ray diffraction technique using Cukα radiation. It appeared that the ZnSe films are hexagonal wurtzite in structure with preferred orientation along <101>. The calculated d-values, intensities of reflections and lattice parameters matched with that of the JCPD data. The calculated particle size decreased with quantity of hydrazine hydrate added in the bath (decrease in Zn/Se ratio). The optical absorption measurements in the range of wavelength from 300-1100 nm showed direct type of transitions with an optical gap decreased from 2.71 eV to 2.60 eV for the change of Zn/Se ratio from 0.993 to 0.571. The surface features revealed by SEM showed that the crystallites are nonuniformly distributed and spherical in shape. From micrographs it is seen that crystallite size decreased with increasing amount of hydrazine hydrate. Some overgrowth like structures (of the same size and shapes) has also been observed at high concentration of hydrazine hydrate.

Keywords: *CBD, Hi-Tech material, hydrazine hydrate, hexagonal wurtzite, spherical crystals.*

Introduction

Polycrystalline zinc selenide is an important technological material suitable for red, blue and green light emitters, thin film transistors, ultrasonic transducers, photo detectors, photovoltaic devices including electrochemical photovoltaic converters, laser screens, etc.[1-7]. It is a II-VI direct gap semiconductor having unique physical properties, viz. wide optical energy gap (2.7 eV), high refractive index and low optical absorbance in the VIS-IR spectral regions, and has been used as an n-type window layer in thin

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film heterojunction solar cells[1-7]. At present CdS is most extensively used buffer layer for high efficiency values in Cu (In, Ga) (S, Se) $_2$ based solar cells. However, due to its toxic nature much attention has been focussed recently on developing Cd-free and environmentally friendly buffer layers. ZnSe is one of the substitutes, which has wider bandgap, smaller lattice mismatch and good conduction band that may transfer high energy photons to the absorber layer of the solar cells[1, 5, 8]. A varieties of techniques have been employed for the formation of good quality thin films. This includes chemical bath deposition[1,6,7,9], metal-organic chemical vapour deposition[10,11], molecular beam epitaxy[2,10,12], atomic layer epitaxy[2], spray pyrolysis[2,13], thermal evaporation[2,14], electrodepostion[2,15], wet chemical method, hot-inject colloid method, sonochemical and solvothermal or hydrothermal method [4] , etc. The deposition of ZnSe thin films from an aqueous solution, such as in chemical bath deposition, is attractive due to the ease of fabrication, low cost and no sophisticated process instrumentation and energy intensive equipments are required[1,16-19]. For growth of ZnSe thin films from solution state, reducing agent has a key role in the film formation process that initializes electroless mechanism process resulting in densely packed, homogenous and adherent films[4, 20, 27]. A liquid phase chemical bath deposition (LPCBD) method, set by us is an excellent technique[9,18,19] and was used to deposit ZnSe thin films under the controlled conditions of temperature, time, pH and varying quantity of hydrazine hydrate, a reducing agent. Composition, structure, surface microstructure and morphology, optical characteristics and some chemical properties have been studied for these as-deposited films.

Experimental Methods

Preparation of the samples

A liquid phase chemical bath deposition (LPCBD) was employed for deposition of the ZnSe thin films[9, 18, 19]. All the chemical precursors were of the analytical grade and used as-recived without further purification. The ZnSe films were obtained onto the spectroscopic grade glass microslides of the dimension 75 mm x 25 mm x 1mm, treated in the nitric acid for more than 12h and then washed with acetone, ethanol and finally rinsed with double distilled water, dried and preserved in a dark desiccators[9]. Zinc sulphate and freshly prepared sodium selenosulphate precursors were used as the sources of Zn^{2+} and Se^{2-} ions, respectively. The sodium selenosulphate was obtained by refluxing 2.5 gm selenium metal powder with 7.5 gm sodium sulphite in 80 ml distilled water for 8h, at 80 °C. Hydrazine hydrate (80%) and ammonia (25%) were used to control the concentration of Zn^{2+} and Se^{-2} ions on the substrate surface and consequently the growth rate of ZnSe. As the growth of the ZnSe films is reported to be dependent on the preparation parameters, e.g. growth temperature, time, pH, precursor concentration, etc., these preparative parameters were optimized initially and then the concentration of hydrazine hydrate was varied and optimized. In our experiment[9], ZnSe films were therefore obtained for a total liquid phase chemical bath of 100 ml. The bath contains 10 ml, 0.5 mol lit^{-1} zinc sulphate, (1-15 ml) 80% hydrazine hydrate, 5 ml 25% ammonia and 20 ml, 0.25 mol lit^{-1} sodium selenosulphate at 70 °C deposition temperature. The deposition time was 210 mins and final pH of the reaction mixture was 10.5 ± 0.2. After deposition, substrates with thin film deposits were taken out from the bath, rinsed with double distilled water, dried in air, and kept in a dark desiccator.

Characterization of the samples

The as-deposited ZnSe films were then characterized through the composition, structure, surface morphology, and optical properties. The film thicknesses were measured by an interferometric technique. The film composition and surface morphology were investigated by the EDS and SEM techniques. A JEOL6360, JED2300 scanning electron microscope was used for these studies. The structure and crystalline nature of the materials was then determined by an X-ray diffraction (XRD) technique (Philips PW-3710, Cu/30kV/15mA) with CuKα line (λ= 1.5406 Å). The 2θ range was from (10° to 90°). The optical absorption measurements were recorded using an UV-VIS spectrophotometer (BIO-AGE UV=VIS 2800 PC), in the 300-1100 nm wavelength range.

Results and Discussion

Reaction mechanism and growth kinetics

The deposition of ZnSe thin film is based on the controlled release of the zinc cations and selenium anions in an alkaline medium[16-19]. A thin layer of ZnSe gets deposited on the glass substrates when the ionic product of Zn^{2+} and Se^{2-} ions exceeds the solubility product ($Ksp=10^{-31}$) of ZnSe in a strong reducing atmosphere. Aqueous ammonia was used as the complexing agent while hydrazine hydrate provides reducing atmosphere for the deposition of ZnSe from selenosulphate baths. Sodium selenosulphate was hydrolyzed in an aqueous alkaline medium (with pH > 7), since at lower pH values selenosulphate immediately decomposes to red Se[6, 21, 22]. The free Se^{-2} ion then reacts with Zn^{2+} to form ZnSe nucleuses which then grow in size with time by condensation of more and more Se^{2-} and Zn^{2+} ions from the solution bulk onto the substrate. We propose the following reactions in two parts[9]:

Part - I

$$Na_2SeSO_3 + \bar{O}H \leftrightarrow Na_2SO_4 + HSe^- \qquad (1)$$

$$HSe^- + \bar{O}H \leftrightarrow H_2O + Se^{2-} \qquad (2)$$

To prevent the fast precipitation of zinc sulphate in an alkaline growth solution, Zn^{2+} ions are complexd with NH_3 (with instability constant $K^0 = 1.8 \times 10^{-5}$).

$$ZnSO_4 \leftrightarrow Zn^{2+} + SO_4^{2-} \qquad (3)$$

$$Zn^{2+} + 4\,NH_3 \leftrightarrow Zn\,(NH_3)_4^{2+}. \qquad (4)$$

The formation of $Zn\,(NH_3)_4^{2+}$ complex inturn reduces the concentration of free Zn^{2+} ions which helps to prevent bulk precipitation of the desired product.

$$Zn\,(NH_3)_4^{2+} + Se^{2-} \rightarrow ZnSe + 4NH_3 \qquad (5)$$

Part – II

$$ZnSO_4 \leftrightarrow Zn^{2+} + SO_4^{2-} \qquad (6)$$

$$2\,SeO_3^{2-} + 4N_2H_4 + 2\,Zn^{2+} \rightarrow 2\,ZnSe\cdot 1/2\,N_2H_4 \downarrow + 3N_2 \uparrow + 6\,H_2O \qquad (7)$$

$$ZnSe\cdot 1/2\,N2H_4 \xrightarrow{\Delta \text{ or } H+} 1/2\,N_2H_4 + ZnSe \text{ (thin solid film).} \qquad (8)$$

The concentration and rate of generation of Se^{2-} and Zn^{2+} ions are determined by the reactions (1, 2) and (3, 4), respectively. As the ZnSe film grows well in strong reducing atmosphere, the quantity of hydrazine hydrate was varied from 2 ml to 15 ml and ZnSe samples were deposited. The final product ZnSe thin films are physically hard, tightly adherent, relatively uniform and diffusely reflecting with light brown tinge in smoky appearance. Fig. 1 shows the thickness variation of the ZnSe film layer with concentration of hydrazine hydrate in bath. Film thickness increased with increase in quantity of hydrazine hydrate in the bath, the reason being increased reduction rate with increased amount of hydrazine hydrate in the bath.

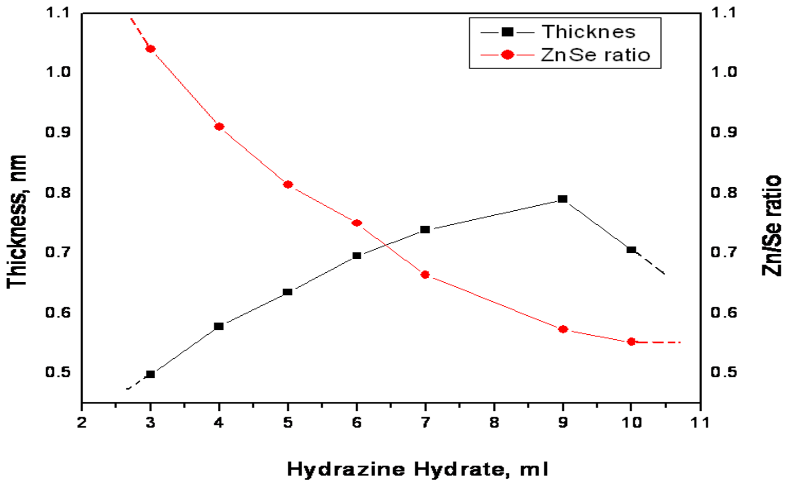

Figure 1. *Variation in ZnSe layer thickness and Zn/Se ratio with quantity of hydrazine hydrate taken in bath.*

Compositional analysis

The as-grown samples were analysed by an EDS analysis technique. As the hydrazine hydrate controls the rate of release of Se^{2-} ions[6,9] , consequently film composition differs from sample to sample. For each of the above sample, an average composition of three different spot locations was considered. Table-1 shows composition of Zn and Se in different ZnSe samples. It appears from the contents of Zn and Se (from table-1) that there is variation of Zn and Se in ZnSe with the added content of hydrazine hydrate in the bath. With addition of hydrazine hydrate in the bath, the Zn content in ZnSe goes on decreasing whereas Se content increased at higher concentration of N_2H_4.

Table 1 shows that for low concentration (quantity) of hydrazine hydrate, sample growth is nearly stiochiometric whereas enhanced rate of reduction at higher concentration of hydrazine hydrate led to non stoichiometric deposits and that non stoichiometry increases further as the ml concentration of hydrazine hydrate in the bath is increased. The average Zn/Se ratio has been calculated from these observations. The general trend is that the ratio Zn/Se decreased with increasing content of hydrazine hydrate in the bath (fig. 1).

Table 1: *An EDS analysis of ZnSe films deposited for various concentration of hydrazine hydrate (P- ml Sample).*

Sample		P3	P4	P5	P6	P7	P9	P10
Mass %	Zn	49.82	49.65	48.88	45.86	44.40	43.63	36.47
	Se	50.18	50.35	51.12	53.14	55.60	56.37	63.53
Zn/Se ratio		0.993	0.98	0.94	0.86	0.79	0.77	0.57

Structural properties

The structure of the good quality samples was determined using the XRD analysis in the 2θ range from 10° to 90° with CuKα radiation (λ= 1.54056 Å). Four typical X-ray diffractograms are shown in fig. 2. The ZnSe samples, at our experimental conditions, are crystalline and display diffraction peaks at different values of 2θ corresponding to the diffraction lines produced by <100>, <101>, <102>, <103>,

<105>, <203>, <112>, <110>, <002>, < 202>, and <210> reflections of hexagonal wurtzite type phase with growth orientation along <101>. One or two metallic Se peaks have also been detected. The d-values and I/I_{max} values are in good consonance with that of the JCPD data[23], however, they follow the same trend of little bit decreasing with increasing N_2H_4 concentration in the bath solution. The ratio c/a remains the same for all the samples. The crystallite sizes were then determined for all the samples using Debye-Scherer relation. The average crystallite size is found to be decreased continuously from 92 nm to 52 nm as the hydrazine hydrate in the bath was varied from 3 ml to 10 ml. Fig. 3 shows variation of the particle size and I/I_{max} with concentration ratio of Zn/Se. The particle size has been found to be decreased with decrease in Zn/Se ratio.

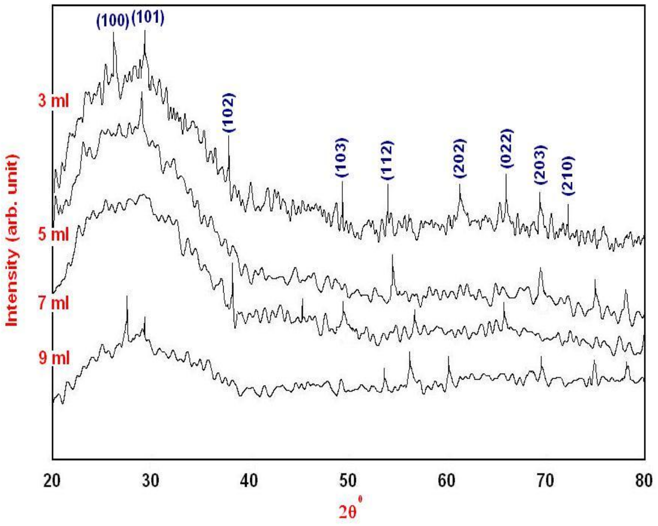

Figure 2. *X-Ray diffractograms for four typical as-deposited ZnSe thin films.*

Optical properties

The fundamental absorption, which corresponds to the transition from valence band to the conduction band, can be used to determine the optical band gap of the material. The optical band gaps were therefore determined for all these films. Figure 4 shows variation of $(\alpha h\nu)^2$ vs. hν for four representative samples. The band gaps were then determined by extrapolating the linear regions of the plots to hν axis. It is seen that the band gap decreased a little (2.7 eV to 2.60 eV) with addition of hydrazine hydrate in the deposition bath (i.e. decreased Zn/Se ratio). The larger band gap for lower concentration of N_2H_4 can be attributed to the presence of the amorphous type phases of ZnSe that have formed the inter crystalline spaces/ voids during deposition. For larger concentration of hydrazine hydrate (decreased Zn/Se ratio), the inter-crystalline spaces/ voids decreased resulting into an increased crystalline nature of the samples thus decreasing the band gap. This is also clear from the SEM micrographs (fig. 5).

Microscopic studies

The surface morphologies of the as-deposited CBD-ZnSe thin films on amorphous glasses, grown under diverse concentration of hydrazine hydrate, were viewed two dimensionally through a scanning electron microscope, (JEOL-6360-JED-2300) at different magnifications so as to get clear insight about the crystal growth and its size. The samples were imaged using a 120 μm x 100 μm area and fig 5 shows few of the micrographs for various Zn/Se ratios. The glass substrates were well covered by the films which are very tightly adherent to the substrate surface and the film surface appears to be rough-diffusely reflecting with presence of the micro pores in them; probably due to the co-deposition of smaller and bit larger clusters together. This is clearly seen from the micrographs (a-e) of the figure 5. In general, it is seen that ZnSe crystallites are clearly distinguishable from each other, almost spherical in shape and distributed non-uniformly (mono-dispersed), with presence of large intercrystalline spacings for low concentration of hydrazine hydrate and then inter crystalline spacing reduced for relatively higher concentration of hydrazine hydrate (fig.5, d and e) with a crystalline growth of bit reduced size. From the micrographs d and e it has been seen that the number of small sized particles reduced significantly favouring the observations that, larger crystallites grow at the expense of smaller ones thus increasing the crystallite density similar to our earlier observations for CdSe[25]. The morphologies further show that the growth of crystalline ZnSe films took place via aggregations of the crystallites, i.e. non homogeneous precipitation of the solution on the glass surface, and that the crystallites formed are of nearly equal in size for higher concentrations of hydrazine hydrate. These observations are in close consance with that reported by Kumar and Singh[24], for ZnSe quantum dots prepared using different precursors. Also careful examination of the micrographs showed that the crystallites tend to unite/agglomerate forming a globule like structures in almost all the causes. The average crystallite sizes were then determined for all the samples. The grain size is found to be decreased from 761 nm to 479 nm as the ml concentration of hydrazine hydrate in reaction bath was increased. It appeared that the estimated grain sizes are larger than that determined from XRD observations, a case normally observed for thin films. The decrease in grain size, at this moment can be understood from the size difference(Zn=1.53 A and Se= 1.22 A) of Zn^{2+} and Se^{2-} and that lower sized Zn^{2+} lattice sites are decreasing with an increasing amount of hydrazine hydrate in bath solution.

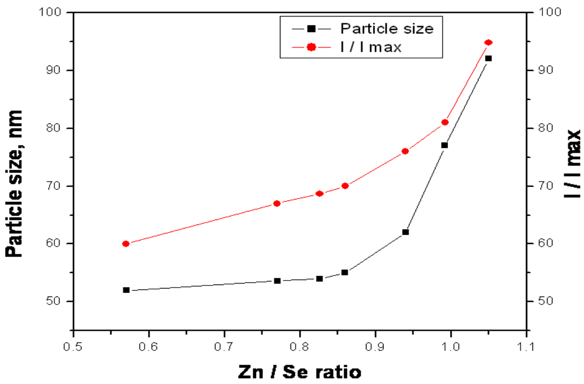

Figure 3. Variation of crystallite size and I/I_{max} with Zn/Se ratio.

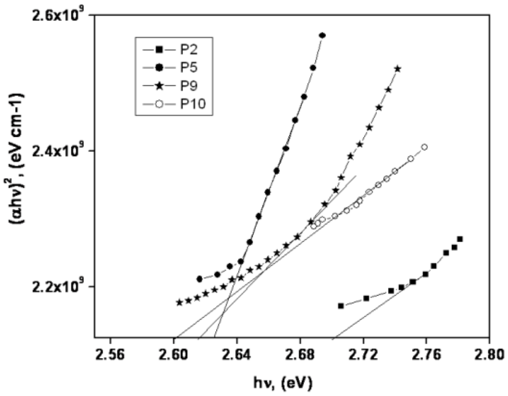

Figure 4. Variation of $(\alpha h\nu)^2$ vs. hν for ZnSe films various Zn/Se ratio.

Conclusions

1. LPCBD technique developed indigenously is used successfully for the deposition of excellent quality ZnSe deposits.
2. Quantity of hydrazine hydrate (reducing agent) has strong influence on the growth of these films.

3. The deposits are relatively uniform, hard sticking to the substrate surface and rough in appearance.
4. An EDS analysis showed that the film stoichiometry decreased with an increase in hydrazine hydrate in chemical bath (Zn/Se ratio decreased).
5. The films exhibited hexagonal wurtzite structure and the crystallite size has been found in the nano range (≈ 50 to 90 nm).
6. As-grown ZnSe exhibited an energy band gap of 2.71 eV, slightly decreased to 2.60 eV with decrease in Zn/Se ratio.

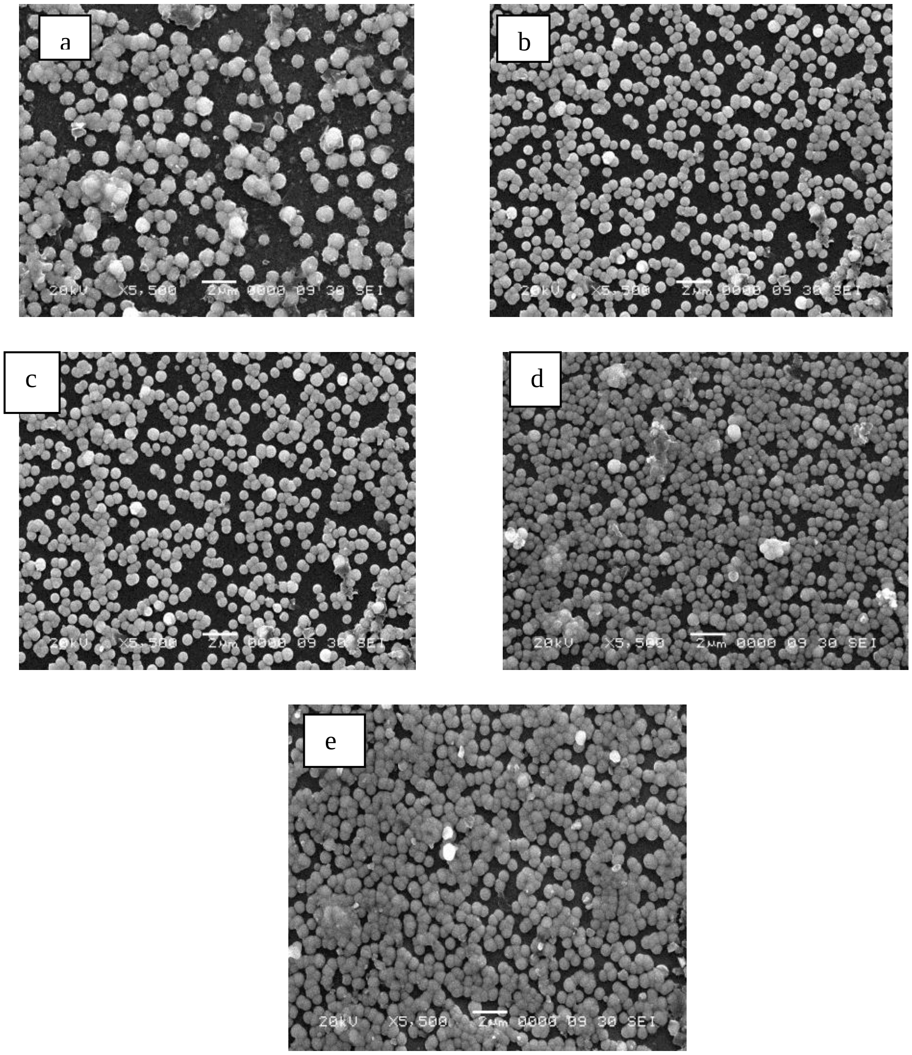

Figure 5. SEM micrographs for ZnSe films of different Zn/Se ratio. a) 0.993, b) 0.94, c) 0.79, d) 0.77, and e) 0.571.

Acknowledgements

One of the authors, Mr. P. C. Pingale, is grateful to UGC, New Delhi, for the award of the Teacher Research Fellowship. Authors (PCP & LPD) also thank Mr. Shinde, University of Pune for the EDS and SEM facilities. Academic discussion with Prof. N. N. Maldar, Polymer Chemistry Department, Solapur University, Solapur is highly acknowledged.

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