Structural, Morphological, Optical and Electrical Properties of Chemically Deposited Thin Films of ZnSe

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Abstract—**Zinc selenide (ZnSe) thin films were grown by inexpensive chemical bath deposition (CBD) method. Thin film deposition was done at bath temperature of 80°C and also this as-deposited film were annealed at 300°C, 400°C and 500°C respectively. The as-deposited film at 80°C cubic phase was retained even after annealing treatment but the crystallinity was improved. The fall in the absorption coefficient is sharper for the films obtained at 80°C Photoluminescence emission peaks of the as-deposited ZnSe thin films were observed at an emission of 425 nm & 470 nm. Depending upon the annealing temperatures, the resistivity value decreased up to 10^2 cm.**
Keywords- chemical bath deposition; semiconductor thin film; optical properties; electrical properties

I. INTRODUCTION

The wide band gap semiconductors are ubiquitous candidates of modern semiconductor technology. Many efforts are currently directed to a new generation of photodiodes based on wide band-gap semiconductors. ZnSe with a direct band gap (Eg = 2.7 eV) is of considerable interest in electronic and optical devices [1-2]. Also it is one of the significant materials used as buffer layer in Cu(In,Ga)Se (CIGS) based thin film solar cells. Compared to CdS buffer layer it has a better conformity of lattice parameter and less toxic [3-6]. Further, it has potential applications in red-blue and green light emitting diodes, photovoltaics, laser screens, thin-film transistors and photoelectrochemical cells. ZnSe thin films have been grown by various techniques such as molecular beam epitaxy, electrochemical deposition, vacuum evaporation, successive ionic layer adsorption and reaction (SILAR) technique, chemical vapour deposition, metal-organic chemical vapour deposition, closed space vapour transport, pulsed laser deposition and sputtering. It was established that structural, electrical and optical properties of these films are very sensitive to deposition conditions and post-deposition heat treatments [6-13]. The preparation method of these films that appears most suitable for the integration in large scale fabrication process is the chemical bath deposition (CBD). The main advantages of the CBD method are it is low cost, non-requirement of sophisticated instruments, low processing temperature and non-polluting nature [14]. This method requires the presence of a reagent that acts as a source of chalcogenide and a complex ion of the metal of interest whose stability equilibrium provides a concentration of metal cation low enough to produce a controlled homogenous precipitation of the film on the solid substrate. However, the CBD process introduces some loose parameters affecting the composition and structure of the buffer layer films, which may determine the performance of the solar device [15]. Different groups have reported different phases such as amorphous, cubic, hexagonal, cubic + hexagonal for ZnSe thin films deposited by CBD method [15-18].

In this present study, we carried out the CBD of ZnSe thin films on non-conducting glass substrates from an aqueous alkaline medium. The as-deposited ZnSe thin films were annealed in an open atmosphere and to study the morphology, structural, optical, emission and electrical properties of chemically deposited ZnSe thin films was discussed.

II. EXPERIMENTAL

A. Growth of ZnSe thin film

ZnSe thin films were deposited onto non-conducting glass substrate from an aqueous alkaline bath (pH=12) using zinc sulphate as Zn^{2+} ion source and sodium selenosulphate as Se^{2-} ion source, ethylenediamine as complexing agent and sodium hydroxide as a pH adjustor. The deposition of ZnSe thin films is based on slow release of Zn^{2+} and Se^{2-} ions in the solution, which then abbreviate onto the substrate. To 10 mL of zinc sulphate (0.5M) solution taken in a beaker of 100 mL capacity, 5 mL of ethylenediamine and 50 ml of de-ionized water were added. The mixture was stirred for 10 min. and the solution pH was adjusted to 12 by adding NaOH solution. The beaker containing the above solution was placed in a constant temperature oil bath maintained at 80ºC. After that the bath solution temperature reached 80ºC, the glass substrate was held vertically in the solution using specially designed sample holder. Then, 10 mL of sodium selenosulphate (0.25M) solution was added to the bath. The solution was continuously stirred and after 2 hrs the slides were removed and washed several times with de-ionized water. The as-deposited ZnSe thin films observed with the naked eye is an orange-yellowish
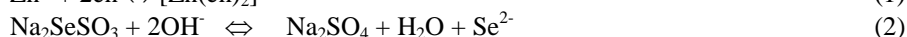
colour. The resultant films were homogenous, well adherent to glass substrate. The as-deposited ZnSe thin films were annealed in open atmosphere at 300ºC, 400ºC and 500°C respectively for 1 h.

B. Characterizations

Phase analysis of the as-deposited and annealed ZnSe thin films was carried out by X-ray diffraction (XRD) studies using a Bruker AXS Diffractometer Plus∕D8 Advanced Spectrometer with Cu K (= 1.5405 Å) radiation with a scan speed of 1° per min. and increment of 0.02°. The optical transmission spectra of the as-deposited and annealed ZnSe thin films were recorded using Shimadzu UV–visible–FIR spectrometer in the range 200–1100 nm. The luminescence properties were investigated by PL Mechelle 900 spectrograph in the range 300–1100 nm using 325 nm He–Cd laser as an excitation source at room temperature. Electrical measurements of the as-deposited and annealed ZnSe thin films were made in the van der Pauw configuration with gold (Au) contacts and the indium soldered platinum wires to the contact plate. Conductivity type, electron mobility and carrier concentration were obtained using Hall Effect measurement apparatus with van der Pauw configuration.

III. RESULTS AND DISCUSSION

Chemical bath deposition of ZnSe thin film occurs by heterogeneous nucleation onto the glass substrate. In the chemical reaction bath, ethylenediamine (en) complexes with Zn^{2+} ions to form water soluble $[Zn(en)_2]^{2+}$ and thus control releasing of Zn^{2+} ion concentration. Sodium selenosulphate and $[Zn(en)_2]^{2+}$ complex dissociate in alkaline medium. The sodium hydroxy reduces the selenosulfate to provide appropriate Se^{2-} ion concentration to permit the formation of ZnSe. At room temperature, it forms a clear solution, no film or precipitate is observed even if the solution is kept for a long time. At low temperature, most of Zn^{2+} ions are in a bound state due to strong Zn-ethylenediamine complex formation and hence there is no precipitation. When the temperature is increased, the kinetic energy increases and as a result decomposition of sodium selenosulfate and zinc complex takes place favouring the formation of ZnSe thin films. The deposition process is based on slow discharge of Zn^{2+} and Se^{2-} ions in the solution, which then summarise either ion by ion or cluster by cluster on the surface of the substrate. The kinetic growth which dictates the formation of ZnSe thin films is according to the following chemical reactions:

$$Zn^{2+} + 2en \Leftrightarrow [Zn(en)_2]^{2+} \tag{1}$$

$$Na_2SeSO_3 + 2OH^- \Leftrightarrow Na_2SO_4 + H_2O + Se^{2-} \tag{2}$$

$$[Zn(en)_2]^{2+} + Se^- \Leftrightarrow ZnSe + 2en \tag{3}$$

At very high deposition temperatures and bath solution pH of 12, homogenous precipitations rather than the film formation occurs due to super saturation. Ethylenediamine is necessary for the formation of ZnSe thin films. The fact that the film formation is observed after the appearance of dense orange-yellowish precipitation in the solution seems to indicate that the film formation is due to the adsorption and aggregation of colloidal particles formed in the solution.

The XRD patterns of the as-deposited ZnSe thin film obtained at 80°C and the corresponding annealed (300°C, 400°C and 500°C) films (Figure 1), we observed a quite sharp peaks corresponding to the cubic phase only suggesting single crystalline nature of ZnSe thin films.
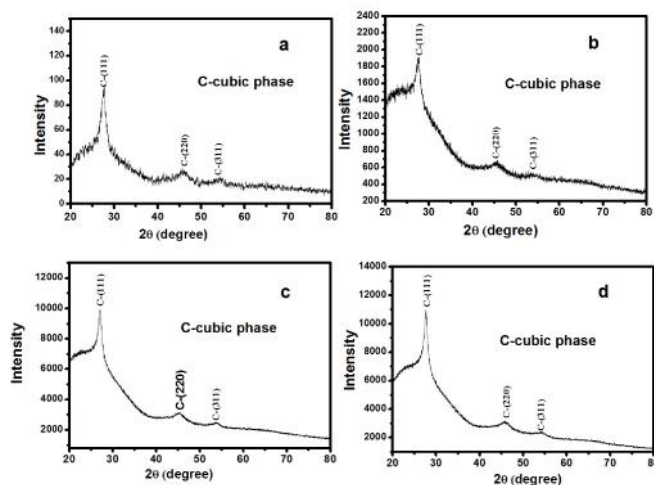

Figure 1 (a-d) XRD patterns of ZnSe thin film (a) as-deposited at 80°C and the same annealed at (b) 300°C (c) 400°C and (d) 500°C.

The films exhibit preferred reflection orientation of (111). Phase transformation from cubic to hexagonal does not occur upon annealing possibly due to the fact that the film grains were less strained. The micro strain

(ε), dislocation density (δ) and number of crystallites per unit area (N) [19-22] were calculated using the following relations (equations (4), (5) and (6). Their values are given in Table 1.

Micro strain (ε) $= \beta \cos\theta/4$ (4)

Dislocation density (δ) $= 15\varepsilon/aD$ (5)

Number of crystallites (N) $= t/D^3$ (6)

where θ is Bragg's angle and t is the thickness of the film. In general, the crystallite size is indirectly proportional to micro strain. The micro strain is found to decrease with increasing thickness (increasing crystallite size) as evident from Table 1. This is obvious due to the layer type grains and its grain boundary which leads to reduction in the concentration of lattice imperfections. The dislocation density is found to decrease continuously with increasing thickness (increasing crystallite size) may be due to the improvement in the crystallinity of the film as well as highly specific orientation along the (111) direction.

Scanning electron microscopy (SEM) is an excellent method to study the morphology of the samples. Figure 2 shows SEM images of the as-deposited and annealed ZnSe thin films. The films were uniform and cover the glass substrate surface uniformly. It is interesting to note that the as-deposited ZnSe thin films seem to be composed of densely packed spherical nanoclusters 300-700 nm in size consisting of a number of spherical nanosized grains. This clearly suggests that the growth of the ZnSe films takes place via cluster by cluster deposition, (i.e.) aggregation of colloidal particles formed in the solution rather than ion by ion deposition. In the annealed ZnSe thin films the clusters are not merged together and we can observe the spherical clusters distributed uniformly over the surface.
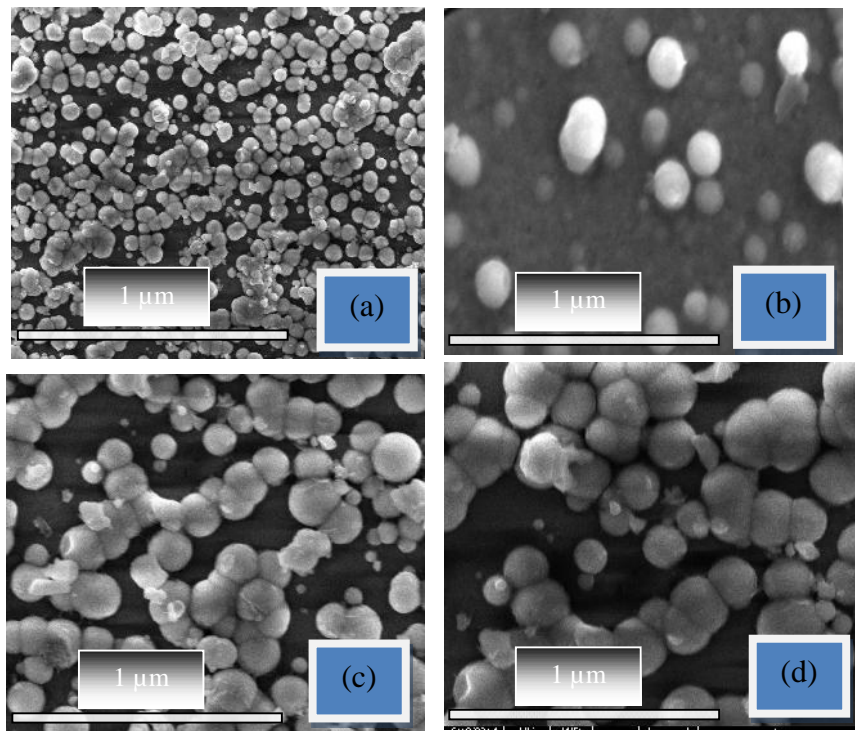

Figure 2 (a-d) SEM micrographs of ZnSe thin film (a) as-deposited at 80°C and the same annealed at (b) 300°C (c) 400°C and (d) 500°C.

Figure 3 shows the plots of $(\alpha h\nu)^2$ vs photon energy (hν) for ZnSe thin films. The as deposited film obtained at 80°C and the corresponding annealed films, which have single cubic phase of ZnSe with stoichiometric composition, show a sharp fall of absorption coefficient with the wavelength of incident radiation at the absorption coefficient edge.

In Figure 4 is shown the room temperature photoluminescence (PL) spectra of the as-deposited and annealed ZnSe thin films. There are two emission peaks centered at 423 nm (2.93 eV) and 470 nm (2.64 eV) for the as-deposited film obtained at 80°C and the same annealed at different temperatures (Figure 3). The strong emission band at 423 nm (2.93 eV) corresponds to the bulk near-band-edge (NBE) emission of ZnSe. The weak emission band at 470 nm is usually assigned to self-activated luminescence, probably due to some donor-acceptor pairs related to Zn/Se vacancies and interstitial states [23-24].
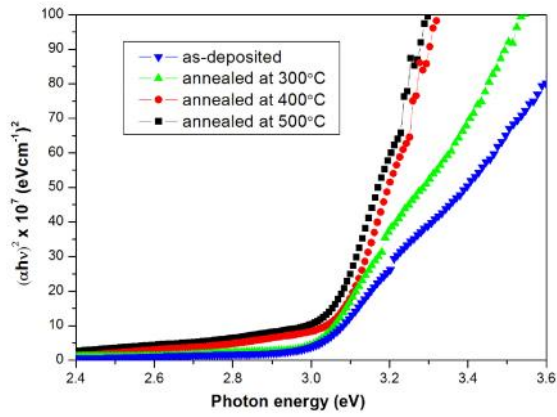
Figure 3   Absorption coefficients vs photon energy curves of as-deposited ZnSe thin film obtained at 80°C and the corresponding annealed thin films
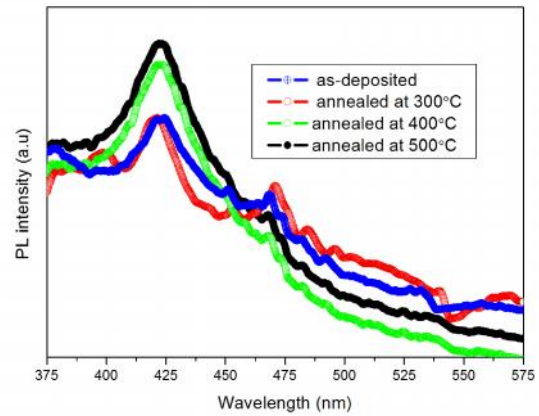
Figure 4   Room temperature photoluminescence spectra of the as-deposited ZnSe thin film obtained at 80°C and the corresponding annealed thin films.

TABLE 1- MICRO STRAIN, DISLOCATION DENSITY, NUMBER OF CRYSTALLITES PER UNIT AREA, BANDGAP, TYPE OF CONDUCTIVITY AND ROOM TEMPERATURE ELECTRICAL PROPERTIES OF THE AS-DEPOSITED AND ANNEALED ZnSe THIN FILMS.

Samples	Micro strain (ν) x 10^{-3}	Dislocation density (υ) x 10^{14} (lines/m^2)	Number of crystallites (N) x 10^{16} (m^{-2})	Band gap (eV)	Type of conductivity	Resistivity (Ωcm)	Carrier concentration x10^{21}(cm^{-3})	Electron mobility ($cm^2V^{-1}s^{-1}$)
As-deposited at 80°C	22.1	57.4	43.4	3.01	N	2.9×10^4	21	42
Annealed at 300°C	21.3	55.6	44.9	2.98	N	1.8×10^3	26	51
Annealed at 400°C	19.6	51.2	48.2	2.96	N	1.2×10^3	30	58
Annealed at 500°C	19.1	50.4	48.1	2.94	N	8×10^2	34	64

Conductivity type, resistivity, carrier concentrations, electron mobility measurements were made for the as-deposited and annealed ZnSe thin films at room temperature by Hall Effect apparatus with van der Pauw configuration. The as-deposited and annealed ZnSe thin films were seen to have n-type conductivity. Resistivity, carrier concentration, electron mobility values of the films are given in the Table 1. The electrical resistivity of as-deposited ZnSe thin film was of the order of 10^4 cm which was decreased to 10^3 cm after annealing. The higher value of resistivity may be attributed to nanocrystalline or amorphous nature of thin film or grain boundary discontinuities, presence of surface states and less roughness of ZnSe films. The electron mobility and carrier concentrations were higher for annealed films compared to the as-deposited films. The higher value of electron mobility and carrier concentrations of annealed ZnSe thin films which leads to a partial screening of the polar vibrations stimulated by mixed phase, improvement in crystallite size and decrease in density of grain boundary intercrystallite of the charge carriers. The grain boundary scattering of charge carriers depends upon crystallite size of grain (i.e) high grain boundary scattering occurs for small crystallite size while low grain boundary scattering occurs for large crystallite size.

In summary, Zinc selenide (ZnSe) thin films have been deposited on non conducting glass substrates by chemical bath deposition technique. In the films made of cubic ZnSe, the crystallites are preferentially oriented with (111) planes. The film deposited at 80°C and the corresponding annealed films are made of pure cubic ZnSe phase. Annealing gives rise to roughness surfaces, due to a weakened film–substrate interaction and more importantly recrystallization.   The fundamental absorption coefficient edge of the as-deposited and annealed ZnSe thin films is different from that of bulk ZnSe due to the creation of defect levels below the conduction band. The as-deposited ZnSe thin films exhibit n-type conductivity. Annealing causes changes in electron mobility and carrier concentration of the ZnSe thin films.

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