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EFFECT OF pH ON THE PHYSICAL PROPERTIES OF $ZnIn_2Se_4$ THIN FILMS GROWN BY CHEMICAL BATH DEPOSITION

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Recently there has been much interest on the preparation and characterization of ternary semiconducting materials, mainly $ZnIn_2Se_4$ (ZIS) due to its potential applications in various fields, particularly as a buffer layer in the fabrication of heterojuction solar cells. In the present work, thin films of ZIS have been synthesized by a simple and economic method, chemical bath deposition at different pH values that vary from 9 *to* 11. *The deposition was carried out for a fixed bath temperature (T_b) of* 90 °*C and constant reaction time of* 60 *min. Ammonia and hydrazine hydrate were used as complexing agents. The chemical and physical properties of the deposited ZIS films were analyzed using appropriate techniques. The X-ray diffraction analysis revealed that the deposited films were polycrystalline and showed* (112) *peak as the preferred orientation. Scanning electron micrographs revealed that the samples had large number of granule like particles in different sizes. The optical transmittance of these samples was found to be* > 75 % *in the visible region and the evaluated energy band gap varied from* 2.15 *eV to* 2.64 *eV with the change of pH value in the range,* 9 - 11. *The detailed study of these results were presented and discussed.*

Keywords: *$ZnIn_2Se_4$, EDAX, XRD, SEM, OPTICAL PROPERTIES.*

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1. INTRODUCTION

The ternary chalcopyrite semiconductors, particularly the Cu-III-VI_2 compounds have proved to be the most potential absorber materials in the fabrication of heterojunction solar cells in terms of conversion efficiency and long-term stability. Among the various combinations of ternary as well as quaternary compounds, $CuInSe_2$ (CIS) and $CuInGaSe_2$ (CIGS) proved to be the successful absorbers and electrical conversion efficiencies > 16 % and 20 % [1] respectively have been achieved at laboratory level using CdS as the buffer and ZnO as the window layers. However, the usage of CdS in photovoltaic cell complicates the in-line process and generates environmental and health problems due to the toxicity of 'Cd' precursor. Alternatively materials such as ZnS, ZnSe, $ZnIn_2Se_4$, In_xSe_y, $Zn_{1-x}Mg_xO$ and $In(OH)_3$, In_2S_3 etc. have been proposed as the substitutes for CdS in CIGS solar cells [2, 3]. Among them, $ZnIn_2Se_4$ (ZIS) is one of the best alternatives for CdS as a buffer layer. As In and Se are already present in ZIS, the problem of lattice mismatch, which is commonly observed in CIS or CIGS-based solar cells can be minimized [4]. Further, ZIS has also potential applications in various other fields such as photoelectronics [5] and electro-optical memory devices [6].

ZIS belongs to the $A^{I}B_2^{II}X_4^{IV}$ defect chalcopyrite family and the first report on $ZnIn_2Se_4$ by Hahn et al., gave the crystallographic data. It crystallizes in the tetragonal structure with the space group of S_4^2, and having the lattice parameters a = 0.569 nm and c = 1.149 nm [7]. Growth of ZIS thin films was first reported by Konagai et al. [8] using three-source co-evaporation of the constituent elements. ZIS layers have been prepared by different chemical and physical methods [9-11]. To our knowledge, there are no reports available on the preparation of ZIS films by chemical bath deposition (CBD) method. In our previous study, we reported on the physical properties and growth mechanism of ZIS films by CBD on glass substrates formed at different bath temperature [12]. In the present study, ZIS films have been grown at different pH values for a constant bath temperature and deposition time by CBD process and the effect of pH on the physical properties are investigated.

2. EXPERIMENTAL

ZIS films were deposited on Corning 7059 glass substrates by chemical bath deposition using 0.05 M aqueous solutions of zinc chloride ($ZnCl_2$), sodium selenite (Na_2SeO_3) and indium tri-chloride ($InCl_3$) as precursors. The deposition bath was prepared by taking 15 ml of aqueous $ZnCl_2$ solution in a separate beaker to which 2 ml of 80 % hydrazine hydrate is added. This makes the solution turbid due to the formation of hydroxides and the turbidity disappears when a few drops of 25 % ammonia is added to the solution bath. 30 ml of $InCl_3$ and 60 ml of sodium selenite precursors are added to the deposition bath in the same sequence. Finally the deposition bath is made-up for a total volume of 120 ml by adding distilled water. The pH of the bath was adjusted to the required value using ammonia and ammonium chloride. The mixture was stirred well using a temperature controllable magnetic stirrer. Ultrasonically cleaned Corning 7059 glass substrates were vertically dipped in the deposition bath while stirring of the solution continues. The deposition of ZIS films is carried out at a fixed bath temperature (T_b) of 90 °C and a reaction time of 60 min by varying the pH value in the range, 9 - 11, measured using DIGITAL pH meter. All the grown films appeared thick brown in color.

The elemental composition of ZIS samples was determined using the FEL Sirion energy dispersive analysis of X-ray (EDAX). The crystallinity of ZIS films was measured using a Siefert X-ray diffractometer (model 3003 TT) with Cu-K_α radiation source (λ = 1.5402 Å) while the surface morphology was evaluated using Zeiss scanning electron microscope (SEM) (model EVO MA 15). The optical transmittance measurements were performed using Hitachi U: 3400 UV-Vis-NIR spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 EDAX Analysis

Fig. 1 shows the chemical composition of ZIS films evaluated using EDAX. The EDAX spectra indicated well defined peaks corresponding to Zn, In and Se in addition to O. All the grown films showed Se deficiency irrespective of the solution pH value. ZIS films deposited at a pH of 11 had Zn: In: Se in the ratio 1:2:3. The deviation in the stoichiometry of the films from 1:2:4

(of $ZnIn_2Se_4$) might be due to the oxygen incorporation during the growth of ZIS films because of the usage of aqueous solutions in the bath or due to the incomplete reaction of the bath mixtures.

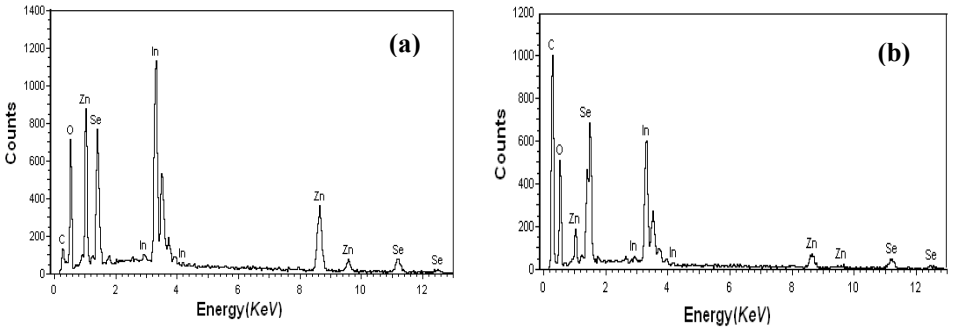

Fig. 1 *– EDAX profiles of ZIS films deposited at (a) pH = 9 and (b) pH = 11*

3.2 Structural Analysis

The X-ray diffraction (XRD) pattern of ZIS films prepared at different pH values are shown in Fig. 2. The XRD spectra of all the ZIS thin films exhibited polycrystalline nature with the tetragonal crystal structure. The diffraction pattern showed two major peaks corresponding to (110) and (112) planes of ZIS in addition to the appearance of a low intensity (204) peak. Further all the peaks were slightly shifted towards higher 2θ values with the increase of pH value. The identified planes in the XRD spectra were in good agreement with the reported data in the literature [13]. No impurity peaks such as Zn (OH), $ZnSeO_3$ etc. were found in the XRD spectra. The intensity of the (112) peak increased with the increase of pH, indicating that more grains were oriented along the (112) plane. This might be due to the formation of more hydroxides at higher pH values that act as nucleation centers and favors hydroxide cluster growth mechanism instead of ion-by-ion deposition.

The average crystallite size, D of the layers was evaluated using the Debye Scherer formula [14].

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

where β is the fringe width at half maximum (FWHM) of the (112) peak, λ is the wavelength of X-rays and θ is the corresponding diffraction angle. The evaluated crystallite size varied in the range, 200 - 350 nm with the change of pH. The degree of preferred orientation corresponding to each plane was studied by the analysis of texture coefficient (C_i), which is a measure of the orientation of each reflection compared to a randomly oriented sample using the following relation [15, 16].

$$C_i = \frac{I/I_0}{(1/n)\sum_{i-1}^{n} I/I_0} \tag{2}$$

where I is measured intensity of the peak in the spectrum, I_0 is the intensity for completely random sample (JCPDS) and n is the number of reflections considered in the analysis. If $C = 1$, it represents the film with randomly oriented crystallites whereas $C > 1$ for films that are oriented preferentially in a particular direction. The variation of texture coefficient with pH value for (112) and (110) peaks is shown in Fig. 3. The value of $C_{(112)}$ increased linearly with the increase of pH value, whereas the value of $C_{(110)}$ was less than that of $C_{(112)}$, implying that the films were highly textured along the (112) direction.

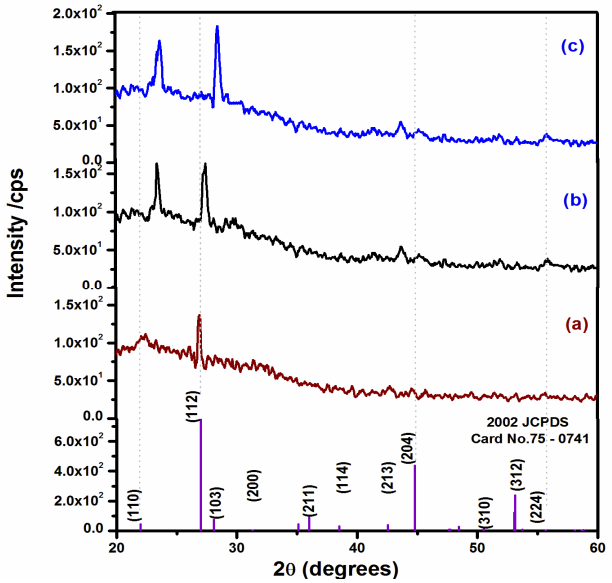

Fig. 2 – *XRD pattern of ZIS films deposited at (a) pH = 9, (b) pH = 10 and (c) pH = 11*

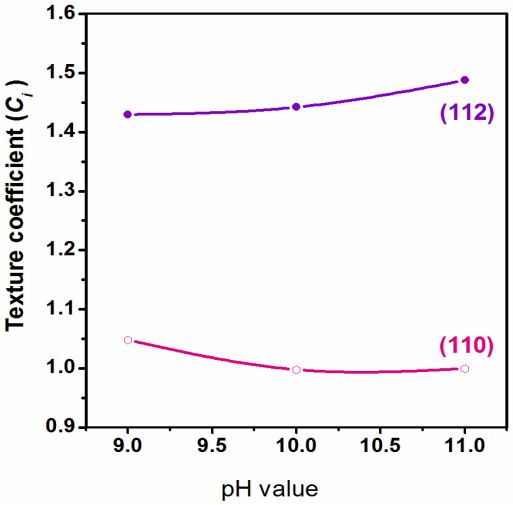

Fig. 3 – *Change of texture coefficient with pH value*

3.3 SEM Analysis

The surface morphology of ZIS films deposited at different pH values was analyzed using the SEM images shown in Fig. 4. The micrographs revealed that the samples had large number of granule like particles with different sizes that were distributed randomly on the substrate surface. The pictures also showed groups of crystallites on an amorphous background. With the increase of pH value these groups join together forming more continuous structure compared to that of the structures grown at lower pH values. Further, the particle size also increased with the increase of pH.

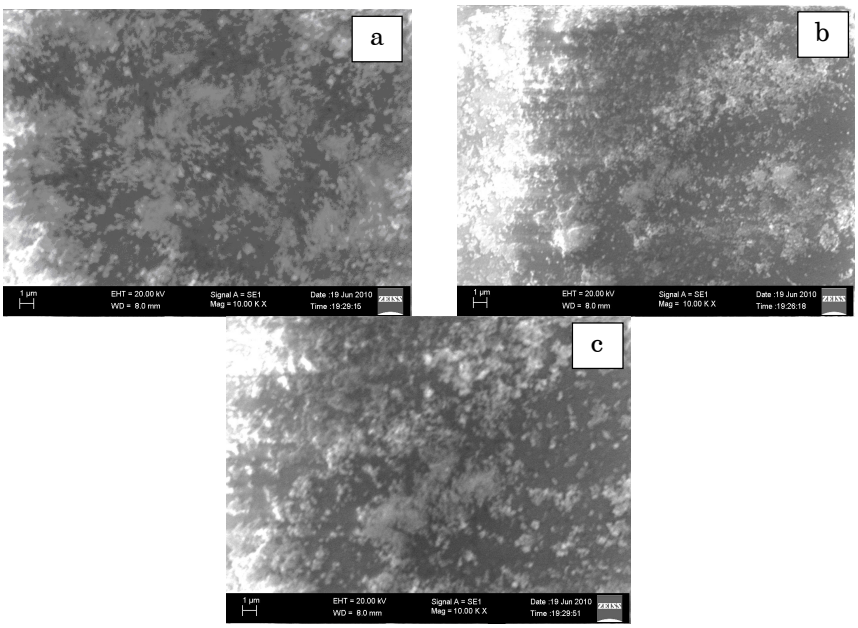

Fig. 4 *– SEM images of ZIS films prepared at pH* = 9 *(a) pH* = 10 *(b) and pH* = 11 *(c)*

3.4 Optical studies

The optical transmittance studies of ZIS films were carried out in the wavelength range, 300 - 2500 nm and the corresponding transmission spectra is shown in Fig. 5. The transmittance of ZIS films increased from 70 % to 80 % above the fundamental absorption edge with increase of pH. It could be observed from Fig. 5 that ZIS films had high transparency in the visible region and showed a steep absorption edge at a wavelength of about 400 - 450 nm, which indicates better crystallinity in ZIS films. It is noteworthy that the absorption edge shifted towards lower wavelength side with the increase of pH, indicating an increase of the energy band gap in ZIS films. The evaluated band gap varied from 2.15 eV to 2.64 eV with the change of pH in the range, 0 - 11, which is in good agreement with the behavior reported by Yadav et al. [9]. The larger energy band gap determined for the films grown at higher pH values might be attributed to the incorporation of hydroxyl groups in the films and/or due to the presence of secondary phases of Zn and Se in small quantity that were not observed in the XRD pattern.

The evaluated refractive index varied in the range 1.85 - 1.73 with change of pH from 9 to 11 and the refractive index values obtained in the present were comparable with the values reported by Gordillo et al. [17] for thermal evaporated ZIS films.

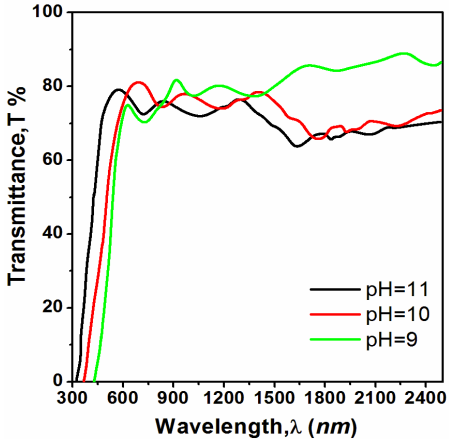

Fig. 5 *– Optical transmittance verses wavelength spectra of ZIS films*

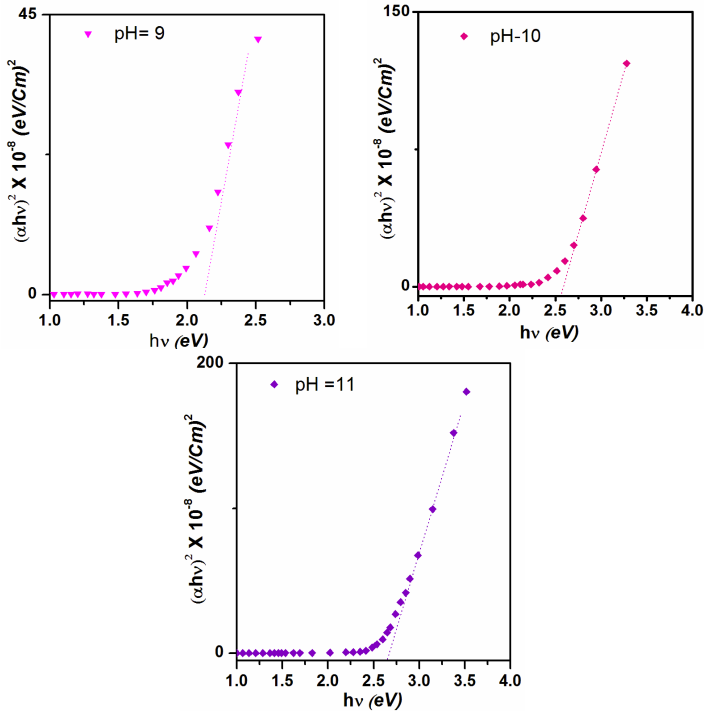

Fig. 6 *– Plots of* $(\alpha h\nu)^2$ *verses hν for ZIS films at different pH value*

4. CONCLUSIONS

$ZnIn_2Se_4$ thin films have been deposited by simple and economic process, chemical bath deposition at different pH values. The pH of the deposition bath varied from 9 to 11 and the layers were grown at a fixed bath temperature (T_b) of 90 °C and a reaction time of 60 min using the ammonia and hydrazine hydrate as complexing agents. The XRD analysis revealed that the deposited films were polycrystalline, exhibiting tetragonal crystal structure and showed the (112) peak as the preferred orientation. SEM micrographs revealed that the samples had large number of granule like particles in different sizes. The optical transmittance of these samples was found to be > 75% in the visible region and the evaluated energy band gap varied from 2.15 eV to 2.64 eV with the change of pH value from 9 to 11.

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