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Precursor Concentration Effect on the Properties of $ZnIn_2Se_4$ Layers Grown by Chemical Bath Deposition

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Abstract

$ZnIn_2Se_4$ (ZIS) films were grown by chemical bath method and the effects of precursor concentration (P_C) on the chemical and physical properties were investigated for the first time. The layers were grown on Corning 7059 glass substrates using equimolar aqueous solutions of zinc chloride, indium tri-chloride and sodium selenite as precursors. The deposition was carried out at different P_C values that vary in the range, 0.01 - 0.075M at a constant bath temperature of 80°C and deposition time of 90 min. The structural studies showed nanocrystalline nature of the films with the (112) preferred orientation. The crystallite size varied in the range, 54 – 125Å. The composition analysis indicated O and Cl in addition to Zn, In and Se in the films. The optical transmittance changed with P_C and layers with P_C=0.05M had the transmittance, >75 % in the visible range. The energy band gap of the films varied in the range, 2.91 - 3.09 eV with change of P_C. FTIR studies were undertaken to identify the adsorbed functional groups on the surface of the films and photoluminescence spectra revealed the presence of defect states in the films. A detailed analysis of these properties are reported and discussed.

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Keywords: $ZnIn_2Se_4$ films, Chemical bath deposition, Physical properties

1. Introduction

$ZnIn_2Se_4$ (ZIS) is a ternary semiconductor that belongs to $A^{II}B_2^{III}X_4^{VI}$ chalcopyrite family. It attracts the attention of many researchers due to its potential application in various fields, including photo-electronics and photovoltaics [1-2]. Photovoltaic devices with the highest conversion efficiency of 15.3% has been reported for $Cu(In,Ga)Se_2$-based solar cells using ZIS as the buffer layer [3]. Investigations on structural, optical and electrical properties of ZIS films grown by various methods such as chemical

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transport reaction, chemical vapor deposition with iodine as the transport agent, spray pyrolysis and thermal evaporation have been reported [4-7]. However, to our knowledge, no attempt has been made to prepare ZIS films by chemical bath deposition (CBD) method. CBD is a simple and low cost technique capable of depositing homogeneous, uniform and smooth layers [8]. Generally, the properties of thin films are highly dependent on the technique used and deposition conditions employed to grow the layers. In the previous work, we studied the effect of pH on the physical properties of CBD grown ZIS films [9]. In this paper, we report, for the first time, on the effect of precursor concentration on the structure, composition, optical properties and photoluminescence of ZIS films prepared by CBD technique.

2. Experimental

ZIS films were deposited on Corning 7059 glass substrates by chemical bath deposition. Aqueous solutions of zinc chloride ($ZnCl_2$), indium tri-chloride ($InCl_3$) and sodium selenite (Na_2SeO_3) are used as the precursor materials for Zn, In and Se respectively. The concentration of all the three solutions was maintained constant for a particular deposition and is termed as 'precursor concentration (P_C)'. The chemical bath is made by mixing 10 ml of $ZnCl_2$, 20 ml of $InCl_3$ and 40 ml of Na_2SeO_3 solutions complexed with 2 ml of (80%) hydrazine hydrate in a separate beaker. Few drops of 25% ammonia (NH_3) are also added to the mixture in order to adjust the pH of the solution to a value, 10. Ultrasonically cleaned glass substrates were dipped into the solution bath vertically while stirring of the solution continues. The deposition was carried out at different precursor concentrations that vary in the range, 0.01 - 0.075M at a constant bath temperature of 80^{o}C and fixed deposition time of 90 min. The crystallinity of ZIS films was measured using a Siefert X-ray diffractometer with Cu-K_α radiation source (λ=1.5402Å). The composition and morphological properties were analyzed using X-ray energy analyzer (Inca Penta FETx3) attached to Zeiss scanning electron microscope (SEM). Optical transmittance studies were performed using Perkin Elmer UV-Vis-NIR spectrophotometer, Fourier transform infrared (FTIR) and photoluminescence (PL) studies made using Thermo Electronic Corporation (IR200 FTIR) and Florolog-3fluorescence spectrometer respectively.

3. Results and discussion

The deposited layers were strongly adherent to the substrate surface and appear brick-red in colour. The thickness of the films, determined by a weighing method was approximately 0.75µm. The chemical composition of the films was evaluated from energy dispersive analysis of X-rays (EDAX) measurement. The EDAX spectra indicated the prominent peaks corresponding to Zn, In and Se in addition to O, C and Cl. The evaluated stoichiometry of the grown films deviated from the 1:2:4 atomic ratio of $ZnIn_2Se_4$, which is mainly due to the incorporation of oxygen, carbon and chlorine into the films during the growth process. In the EDAX spectra, the peaks of 'In' are more pronounced when compared to the other elements. This might be due to the presence of insoluble $In(OH)_3$ in minute quantity on the film surface. The appearance of oxygen in the EDAX spectra might be due to the presence of oxygen in the aqueous solutions of precursors used for the film deposition [10] and /or incomplete reaction of the bath mixtures.

The X-ray diffraction (XRD) spectra of all ZIS films grown at various P_C values showed a strong (112) orientation, exhibiting the tetragonal crystal structure. The spectra also showed four major peaks related to the (110), (200) and (211) planes in addition to low intensity (103), (213), (204) and (310) planes that correspond to the orientations of $ZnIn_2Se_4$. No other peaks related to binary phases of Zn-Se and In-Se were observed. These results are in agreement with the JCPDS and other reported data [11, 12]. Fig. 1(a) shows the typical XRD spectrum of ZIS film formed at P_C=0.05M. All the films also showed