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Characterization of CBD deposited $CuInSe_2$ thin film

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ABSTRACT

Ternary $CuInSe_2$ chalcopyrite semiconductor thin films have been deposited on glass slide substrates by chemical bath deposition technique. The chemical composition of the as-deposited thin film by energy dispersive analysis of X-ray technique showed the film to be near stoichiometric. The X-ray diffraction analysis of the thin film confirmed the tetragonal unit cell structure. All the obtained lattice parameters were in good agreement with the reported data. The crystallite size determined by Scherrer's formula and Hall-Williamsons relation using X-ray diffraction data were in good agreement with each other. The microtopograph study of the as-deposited thin film surfaces by optical and scanning electron microscopy showed that the thin film uniformly covers the entire substrate surface. The atomic force microscopy of the thin film surface showed grains and coalescence between them. The as-deposited thin film possesses direct optical bandgap having value of 1.39 eV being analyzed by Ultra violet-Visible-Near infra red spectroscopy. The optical parameters like reflectance *R*, transmittance *T* variation with wavelength and extinction coefficient *k*, dielectric constant ε_c and refractive index η variation with incident photons hν showed the as-deposited thin film can be used as an absorber in the visible region of spectrum. The electrical transport properties study confirmed the semiconducting and p-type nature of the as-deposited thin film. The obtained results are comprehensively discussed in this paper.

1. Introduction

The ternary compound semiconductors belonging to the I–III–VI_2 (I = Cu, Ag; III = In, Ga, Al; VI = S, Se, Te) family has attracted potential interest due to their significant semiconducting, electrical, structural, mechanical and optical properties [1–6]. They crystallize in tetragonal chalcopyrite structure. Of the all chalcopyrite semiconductors, $CuInSe_2$ (CIS) and $Cu(In,Ga)Se_2$ (CIGS), has been most extensively studied due to their properties suitable for optoelectronic applications [7,8]. Among the two potential chalcopyrites, the CIS has a direct bandgap of 1.05 eV [9]. The bandgap can be tuned between 1 and 2.4 eV by adjusting indium and selenium atomic compositions [10], thus making it most suitable for solar energy harnessing. The other advantage of CIS is that it can be obtained in both n- and p-type. The optical absorption coefficient is large, of the order of $10^5\ cm^{-1}$, nearly double to that of amorphous and crystalline silicon [11]. Because of their large optical absorption coefficient, a thickness of 1.5–2 μm is sufficient to absorb the useful portion of the solar spectrum [12–14], thus enhancing CIS thin films prospective. The CIS are less affected by the cosmic radiations, making it suitable for extra-terrestrial applications [15]. The above all properties and characteristics of CIS attracted the authors to choose the compound. The authors deposited $CuInSe_2$ thin films by simple chemical bath deposition (CBD) technique. The deposited thin film was comprehensively characterized for their chemical composition, crystal structure, surface microtopography, optical properties, electrical transport properties, etc.

2. Experimental

2.1. Thin films deposition

In the present study, the chemicals used for the synthesis of $CuInSe_2$ thin films are; cupric chloride dihydrate ($CuCl_2{\cdot}2H_2O$) [purity 98%, Astron Chemicals, India], indium(III) chloride anhydrous ($InCl_3$) [purity 99.99%, Alfa Aesar, A Johnson Matthey Company, U.S.A], triethanolamine (TEA) ($C_6H_{15}NO_3$) [purity 99%, Astron Chemicals, India], elemental selenium (Se) [purity 99%, SISCO Chem Pvt. Ltd., Mumbai, India], sodium sulfite (Na_2SO_3) [purity98% Alfa Aesar, A Johnson Matthey Company, U.S.A] and hydrochloric acid (HCl) (35% pure). All the chemicals were of AR grade and were used as received without any processing or purification. All chemicals were stored in evacuated desiccators to prevent degradation due to atmosphere or

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humidity.

Starting solutions were prepared by dissolving requisite amount of respective elements in double distilled water. The Cu^{2+} ion solution was prepared using $CuCl_2{\cdot}2H_2O$ and In^{3+} ion solution was prepared by $InCl_3$. The Se^{2-} ion solution was prepared using Na_2SO_3 and elemental Se. The 1 M Na_2SeSO_3 was prepared by refluxing 7.90 g of elemental Se with 12.60 g of Na_2SO_3 in 100 ml of double distilled water for 8 h at 90 °C temperature. The reaction leading to the formation of Na_2SeSO_3 is;

$$Se + Na_2SO_3 \rightarrow Na_2SeSO_3$$

The TEA ($C_6H_{15}NO_3$) acts as a complexing agent to control the slow release of ions so that immediate agglomeration does not happen. The HCl is added to set the pH of the solution. After preparation of above precursor solutions, deposition of $CuInSe_2$ thin films was carried out as below.

The solution for the deposition of $CuInSe_2$ thin film by CBD technique was prepared by firstly taking 5 ml of 0.55 M $CuCl_2{\cdot}2H_2O$ solution in a 100 ml clean dry glass beaker. To it was added 5 ml of 0.1 M TEA ($C_6H_{15}NO_3$) solution. The addition was done under continuous magnetic stirring and continued for 5 min. Then to the mixture, 5 ml of 0.55 M $InCl_3$ was added. The addition was done under continuous stirring. The stirring was carried out for 10 min. After that 5 ml of 1 M Na_2SeSO_3 was mixed slowly under stirring. Lastly, 5 ml of 0.1 M HCl was added to the mixture and stirred for 5 min. At last 50 ml of double distilled water was added to make the final solution 75 ml in volume. The pH of the final bath solution was measured and was found to be 4. The pre-cleaned glass slide substrate was immersed in the bath solution and kept vertical in the beaker containing final solution for thin film deposition to occur. The glass slide substrates used for deposition were laboratory grade glass slides having dimensions as 76 mm × 26 mm × 1 mm [Plaza Industrial Corporation, Delhi, India]. The procedure adopted for cleaning of the glass slides was; firstly the slides were thoroughly washed with detergent and dried in air. The air dried slides were then dipped in concentrated hydrochloric acid and were kept immersed for 24 h. After 24 h acid dip, the slides were removed and were given multiple wash with double distilled water. The water was allowed to drain off and the slides were air dried. The perfectly dried slides were finally given ultrasonication in acetone for 10 min. Lastly, the glass slides were kept in an oven by maintaining it at 80 °C till used for deposition of thin films. The deposition was carried out at room temperature for 3 h. The glass slide with deposited thin film was removed from the solution, rinsed with double distilled water and allowed air drying.

2.2. Characterization techniques

The chemical composition of the as-deposited $CuInSe_2$ thin films was determined by energy dispersive analysis of X-ray (EDAX) technique attached to scanning electron microscope, XL 30 ESEM operated at 30 kV. The crystal structure of the as-deposited $CuInSe_2$ thin films formed on glass substrate at room temperature was determined by X-ray diffraction (XRD) technique, Rigaku Miniflex employing CuK_α radiation. The surface microstructures of the thin film were examined under 'Epignost', Carl Zeiss Jena GmbH, West Germany optical microscope and above mentioned scanning electron microscope (SEM). The detailed surface morphology of the thin film deposited at room temperature was studied using an atomic force microscope (AFM), Nano Surf easy Scan 2 in tapping mode. The optical absorbance measurement of the thin film-glass substrate combination were recorded with unpolarized light at normal incidence in the wavelength range of 200–2000 nm using UV–vis–NIR Spectrophotometer Perkin-Elmer Lambda-19 equipped with deuterium-tungsten lamp and photomultiplier tube with PbS detectors. The substrate contribution to the optical absorbance was corrected by introducing an uncoated substrate in the reference beam. The four-probe technique employing Four probe setup Model-DFP-02, SES Instruments Pvt. Ltd., Roorkee, India make was used for measuring the electrical resistivity variation with temperature. Hall effect measurement at room temperature was carried out employing 14 kG electromagnet using van der Pauw geometry employing the Hall effect set-up Model-DHE-22 using constant current source Model-DPS175 developed by SES Instruments Pvt. Ltd., Roorkee, India.

3. Results and discussion

3.1. Thin film deposition

The separate cationic precursor solution consisted of two parts: the copper precursor solution was 0.55 M $CuCl_2{\cdot}2H_2O$ and the indium precursor solution was 0.55 M $InCl_3$. The anionic source for selenium was 1 M Na_2SeSO_3 solution. The pH of the solution was maintained at 4 by addition of 0.1 M of HCl. The HCl is a strong acid which dissociates fully and helps in reaction bath protonation. Here TEA acts as a complexing agent to ensure slow release of Cu ions in the deposition mixture. The base constant K_b of TEA is 5.75×10^{-7} at ambient temperature [16] meaning that the nitrogen atoms of TEA are substantially protonated by hydrogen ions in the pH region of the present reaction condition. The formation or complexing constant of $[Cu(TEA)_2]^{2+}$ is 1×10^6 [16], stating to be too high. In the chemical bath, Cu^{2+} ions released from the $[Cu(TEA)_2]^{2+}$ were reduced to Cu^+ ions due to the presence of excess sodium sulfite according to below reactions [17,18],

$$CuCl_2{\cdot}2H_2O \rightarrow Cu^{2+} + 2Cl^-$$

$$CuCl_2{\cdot}2H_2O + TEA \rightarrow [Cu(TEA)_2]^{2+} + 2HCl + 2OH^-$$

$$[Cu(TEA)_2]^{2+} \rightarrow Cu^{2+} + TEA$$

$$SO_3^{2-} + 2OH^- \rightarrow SO_4^{2-} + H_2O + e^-$$

$$Cu^{2+} + e^- \rightarrow Cu^+$$

Se^{2-} ions are released from the sodium selenosulphate solution [19],

$$Na_2SeSO_3 + OH^- \rightarrow Na_2SO_4 + HSe^-$$

$$HSe^- + OH^- \rightarrow H_2O + Se^{2-}$$

The excess sodium sulfite over selenium prevents the oxidation of selenium and facilitate in re-precipitation as selenium [20]. The overall reaction for the formation of $CuInSe_2$ is thus,

$$Cu^+ + In^{3+} + 2Se^{2-} \rightarrow CuInSe_2$$

The thickness of the CBD as-deposited $CuInSe_2$ thin film was determined by the standard gravimetric method [17,21]. In the thickness calculation, the density of the $CuInSe_2$ was taken that of the bulk as 5.77 g cm^{-3} [22].

3.2. Chemical composition

The chemical composition of the as-deposited $CuInSe_2$ thin film was estimated by recording its EDAX spectrum. The Fig. 1 shows the EDAX

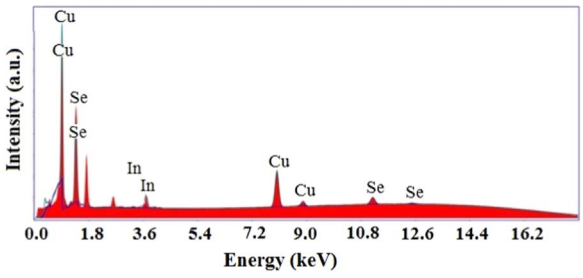

Fig. 1. The EDAX spectrum of $CuInSe_2$ thin film.