Properties of CuSbS$_2$ thin films electrodeposited from ionic liquids as p-type absorber for photovoltaic solar cells

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ABSTRACT

Electrodeposition of CuSbS$_2$ semiconductor thin films for photovoltaic solar cells is investigated from ionic liquid electrolyte based on choline chloride–urea eutectic. Cyclic voltammetry study shows Cu and Sb deposition potential of −0.54 V and −0.48 V vs Pt, respectively. Highly crystalline CuSbS$_2$ films in the chalcostibite orthorhombic structure without binary compound phases are electrodeposited at a potential of −0.65 V vs Pt with Cu to Sb precursor ratio of 1:1 and Na$_2$S$_2$O$_3$ as sulfur source in ionic liquid medium held at 80 °C. Increase in Cu-precursor ratio (1:0.71) led to Cu$_3$SbS$_3$ ternary and that of Sb-precursor ratio (1:1.4) led to binary Sb$_2$S$_3$ phase inclusion in the phase field of the CuSbS$_2$ films. Electrochemical impedance spectroscopy studies show diffusive ionic transport limited growth mechanism. Single phase CuSbS$_2$ films show direct band gap energy of 1.66 ± 0.01 eV and films with inclusive secondary phases have band gap energy of 1.73 ± 0.01 eV. As-deposited CuSbS$_2$ films are p-type and a hetero-junction in the nZnO–pCuSbS$_2$ structure showed rectifying current–voltage behavior and low reverse current consistent with compact pinhole free CuSbS$_2$ film synthesized by ionic liquid electrodeposition.

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1. Introduction

Thin films of diverse ternary Cu-based chalcogenide semiconductors represented by a general formula Cu$_x$BX$_y$ (with B = Bi, Sn, Sb and X = S, Se, Te) are being actively investigated as new class of p-type photo-absorber layers for conventional thin film solar cells which are based on the non-toxic, earth abundant and low cost materials [1–12]. These semiconductors have the potential to substitute for rare and expensive In and Ga in the more extensively studied and proven thin film solar cells based on absorbers such as CuIn$_{1−x}$Ga$_x$S$_{2−y}$Se$_y$ (CIGS) [13]. The CIGS solar cells offered a solution to the Cu-diffusion issue [14] in the first generation thin film pCu$_2$S:nCdS solar cells [15] by introducing In and Ga. In this context Cu–Sb–S system particularly, the CuSbS$_2$ thin films are important as these belong to the similar I.V.VI$_2$ group as CIGS (I.III.VI$_2$) and Sb being isovalent with In while having similar ionic radii as that of In can prove to be an ideal substitute for In in CIGS category of cells. The fundamental band gap of CuSbS$_2$ appears to be a direct one and a stronger photo-absorption is expected due to high absorption coefficient, both attributes are relevant for use in photovoltaic solar cells. Though lacking in agreement, the reported CuSbS$_2$ band gap energy in the range 1.38–1.56 eV [6,8,9] is close to optimum value required for solar cells and can be tuned in by the addition of Se [8]. Basic knowledge of the electronic and crystal structure and optical band gap properties of CuSbS$_2$ is derived from theoretical

analysis [1] and from the bulk single crystals synthesized by solvothermal technique [6]. The electronic and optical properties including the band gap of CuSbS$_2$ films being sensitive to the thin film preparatory methods have not been fully explored and established for use as a photo-absorber in thin film solar cells.

The synthesis of CuSbS$_2$ thin films has been reported by a variety of direct and indirect methods. The direct approaches for CuSbS$_2$ film formation widely used are spray pyrolysis [3,16], and thermal evaporation [7,17]. Chemical spray pyrolysis of aqueous solution comprising of Cu and Sb inorganic salts and thiourea at ~350 °C has been shown to form CuSbS$_2$ films and though the effect of precursor composition and the additives on morphology and band-gap has been reported, a control of these parameters is critical in order to exclude the secondary phases [3,16]. The effect of these parameters on photovoltaic properties in the TiO$_2$/CuSbS$_2$ heterostructure device has also been analyzed [18]. The vacuum deposition method is based on thermal evaporation of alloyed material resulting in films with mixed CuSbS$_2$ and Sb$_2$S$_3$ phases which reflect on the optical band-gap properties and require a post-deposition vacuum annealing step to crystallize a CuSbS$_2$ phase [7,17]. The indirect methods are more widely studied and use a two-step approach involving diffusion/reaction from vapor phase or in solid-state among constituent binary compounds. It was demonstrated that CuSbS$_2$ films can be formed by annealing vacuum deposited Cu/Sb stacks and Cu–Sb alloyed precursors in the presence of chalcogen (S, Se) vapor [8]. Here, the differential kinetics of Cu and Sb requires high (≥350 °C) temperature processing and a control of heating rates to avoid binary phase separation. Such an approach has been

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used in the past to fabricate high efficiency Cu_2ZnSnS_4 (CZTS) solar cell absorber layers [19,20]. Recently, $CuSbS_2$ thin films by sulfurization of the electrodeposited Cu–Sb stacks in H_2S at 450 °C have been deposited on Mo coated substrates and using a CdS buffer layer in a similar solar cell structure as that of the CZTS, a 3.1% efficiency solar cell device has been demonstrated [21]. Yet another approach reported earlier is by thermally induced solid-state reaction at ~400 °C between chemically deposited binary CuS and Sb_2S_3 compound layers wherein the thickness and temperature conditions of reacting films are critical to the synthesis of single phase $CuSbS_2$ films [9]. Thus formed p-type $CuSbS_2$ films in the p-i-n solar cell structure with i-Sb_2S_3 and n-CdS have shown, $V_{OC} = 0.345$ V and $J_{SC} = 0.2$ mA·cm^{-2} [22]. Another variant of interlayer diffusion reaction studied for forming the $CuSbS_2$ film is between the chemical bath deposited Sb_2S_3 film and vacuum evaporated Cu thin film which shows Cu-layer thickness dependent changes in the photoconductivity and band-gap of the final film [10].

Electrochemical deposition technique for the synthesis of semiconductor films for solar cells holds considerable promise due to its scalability and low cost potential. Electrodeposition under galvanostatic, potentiostatic and pulsed current techniques for the synthesis of thin films of binary semiconductors mainly, CdS [23,24], CdSe [25], CdTe [26,27] and Bi_2Te_3 [28] has been widely employed in the past for the fabrication of thin film solar cells. Conventionally, the electrodeposition of semiconductor films has been carried out from aqueous or organic electrolytes. The electrodeposition in an aqueous acidic [29,30] or ammonia electrolyte [31], has issues like corrosion, hydrogen evolution and oxidation of metal precursors which adversely affect the semiconducting properties of films for use in solar cells. The organic medium electrodeposition of semiconductors like CdTe films [32,33] somewhat mitigates these issues but has found limited application in solar cell fabrication as these solvents are both expensive and toxic. Another class of electrolyte usually referred to as ionic liquids has been investigated for electrodeposition [34,35]. Ionic liquids are characterized to have higher ionic conductivity, a large electrochemical potential window of stability, and low vapor pressure even at high temperatures. There have been several reports using ionic liquid electrolytes for electroplating of various metals and alloys [36], but fewer for electrodeposition of semiconductors.

In the context of synthesis of thin films of semiconductors useful for photovoltaic solar cells, electrodeposition from the ionic liquid electrolytes offers a better perspective. Large electrochemical window can allow deposition at more negative potentials which enable higher deposition rates and composition control without interference from H_2 evolution at cathode. Enabling electrodeposition at high temperature is significant in promoting crystalline character of films and higher ionic conductivity compared to aqueous or organic medium saves energy in the deposition process. However, these merits of ionic liquid medium have not been sufficiently exploited in the electrodeposition of semiconductor films as evidenced from scarce research publications. Early work on the formation of CdTe thin films has been reported by electrodeposition from ionic liquid based on 1-ethyl-3 methylimidazolium Chloride:tetrafluoroboarate molten salts [37] and CdS from phosphonium ionic liquids [38]. A simpler and cost effective eutectic ionic liquid system based on choline chloride with hydrogen bond donor species glycol or amides as well with urea have been described by Abbott et al. [39] and have been employed in the electrodeposition of zinc–tin alloy films [36]. Using choline chloride (ChCl) and urea eutectic mixture (commercial name Reline) as electrolyte, the thin films of binary semiconductors, CdTe [40], CdS, CdSe [41] Bi–Te and Sb–Te [42,43] have been electrodeposited. Except for the Cu–In–Ga–Se precursor system which after selenization forms $Cu(InGa)Se_2$ films [44], direct electrodeposition of thin film of ternary semiconductors like $CuSbS_2$ from ionic liquid electrolyte for solar photovoltaic absorber application is rare. Such electrolyte besides being biodegradable and nontoxic is highly stable enabling multiple film depositions which is important for large area of inexpensive solar cell fabrication. This paper reports on the single-step electrochemical deposition and structural, optical and p–n junction properties of $CuSbS_2$ thin films deposited from ChCl–urea eutectic based ionic liquids.

2. Experimental details

The ionic liquid electrolytic medium was prepared by heating a mixture of 1 mol choline chloride ($C_5H_{12}ONCl$)) and 2 mol urea ((NH_2)$_2$ CO) to 80 °C while thoroughly stirring under N_2 blanket until a clear transparent liquid is obtained [36,39]. For the electrodeposition of $CuSbS_2$ films, Cu^{2+} and Sb^{3+} ions were derived from anhydrous salts $CuCl_2$ (99% Sigma Aldrich) and $SbCl_3$ (≥99% Sigma Aldrich), respectively which were dissolved in desired molar concentrations in the ChCl–urea electrolyte. For electrodeposition experiments, the molar proportions of these compounds corresponded to Cu to Sb precursor concentration of 1:1; 1:1.4; and 1:0.71 representing stoichiometric, Sb excess and Cu excess compositions, respectively. The sulfur ions required for ternary compound film formation were sourced by dissolving 10 mM sodium thiosulfate, $Na_2S_2O_3$ (99% Sigma Aldrich) to the clear ChCl–urea solution containing $CuCl_2$ and $SbCl_3$. The electrodeposition of films as well as electrochemical characterizations was done in a three-electrode electrochemical cell. The substrate for film growth was fluorine doped tin oxide (FTO) coated transparent conducting glass (TCO) of nominal sheet resistance 10 Ω/□ which forms a cathode. The counter electrode was a polished and cleaned Pt foil. A Pt wire in direct contact with the electrolyte served as a pseudo-reference electrode. The electrodes were connected to Solartron potentiostat/galvanostat (model 1287A) controlled with Corrware program to perform cyclic voltammetry (CV) at scan rates of 5 − 100 mV · s^{-1} and potentiostatic electrodeposition of films at −0.6 to – 0.7 V vs. Pt. All electrodepositions of films were done in electrolyte solution with precursors held at 80 °C for periods varying from 30 to 75 min under potentiostatic conditions. Subsequently, the deposited films were washed with deionized water to remove adhering viscous electrolyte and dried under N_2 flow. The electrochemical impedance spectroscopy (EIS) measurements were done in the frequency range 100 mHz–1 MHz with ac voltage amplitude of ± 10 mV using Solartron gain phase analyzer (model 1260A) driven by Z-Plot software. The measured data in the form of Nyquist and Bode–Bode plot were analyzed on the basis of equivalent electrical circuit model consisting of parallel R–C circuit with a series resistance representing charge transfer, constant phase element and electrolyte resistance, respectively.

The structural, optical and structural characterizations of films were done in the as-electrodeposited state without any post-growth high temperature treatments. The microstructure of films was studied using a Zeiss Supra 55 field emission scanning electron microscope (FESEM) operating at an acceleration voltage of 10 kV. The crystalline structure of the thin films was determined by X-ray diffraction (XRD) analysis using PANalytical's X'Pert PRO Materials Research diffractometer with Cu Kα radiation using a Ni filter. The diffractometer was initially calibrated with thin film for 2θ and ω axis positions. The z axis was calibrated such that the diffraction pattern is obtained from thin film region. The diffraction pattern was recorded in the θ–2θ scan mode in which the sample moves by the angle θ and the diffracted X-ray intensity are recorded at 2θ angle by simultaneously moving the detector. The XRD pattern recorded in the required 2θ range is compared with international center for diffraction data (ICDD) database containing reference patterns in order to identify the crystalline structure and phases present in the film. The optical transmission measurements were carried out using Angstrom spectrophotometer in the 300–1000 nm range which provides the film transmittance T_f after accounting for the reflection and substrate losses and compares with transmission T_0 without a sample. A p–n junction diode structure is formed by a sputter deposited 50 nm thick n-ZnO film over a 600 nm thick $CuSbS_2$ film on