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Experimental investigation of the effect of indium content on the $CuIn_5S_8$ electrodes using electrochemical impedance spectroscopy

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ABSTRACT

This paper reports on the use of electrochemical impedance spectroscopy to investigate the electrochemical behavior of spinel $CuIn_5S_8$/electrolyte interface. The $CuIn_5S_8$ spinel films have been potentiostatically deposited onto indium tin oxide (ITO)-coated glass substrate. $CuCl_2$ and $InCl_3$ mixed solutions with different [Cu]/[In] ratios were used as cation precursor and $Na_2S_2O_3$ as the anion precursor in acidic solution and at room temperature. The effect of the [Cu]/[In] ratio in the precursor solution on the structural, chemical stoichiometry, and morphological properties of prepared samples, as well as the electrochemical behavior of the $CuIn_5S_8$/electrolyte interface was investigated. The electrochemical impedance spectroscopy data have been modeled using an equivalent circuit approach. Several parameters such as, flat-band potential and free carrier concentration were determined by the change in the Mott–Schottky plots.

1. Introduction

I–III–VI ternary semiconductors with the general formulae of I–III–VI_2 and I–III_5–VI_8 have potential as photo absorbers in solar cells, optoelectronics devices, and photoelectrochemical cells. These ternary semiconductor materials can be prepared to have either *n*- or *p*-type conductivity, depending on the synthesis methods and the composition of elements in samples [4,5]. For applications of solar energy conversion, $CuIn_5S_8$ semiconductor has a suitable band gap to be a photo-absorber in solar or photoelectrochemical cells [1–3]. Furthermore, this material does not contain toxic elements like Se and Ga, which is an advantage in comparison with the other absorbers like $CuInSe_2$ and $CuGa(In)Se_2$. This ternary compound belongs to the $CuIn_{2n+1}S_{3n+2}$ family with $n=2$, and is formed in the in-rich side of the pseudo-binary Cu_2S–In_2S_3 system [9]. At the extreme limits of structural tolerance to off-stochiometry of chalcopyrite phases, this compound stabilizes due to the ordering of the neutral defect pairs ($2V_{Cu}^{-1} + In_{Cu}^{2+}$) and ($2Cu_{In}^{-2} + In_{Cu}^{2+}$) in the Cu–In–$VI_2$ phase [46]. $CuIn_5S_8$ is a cubic spinel with indium found principally on octahedral sites rather than on tetrahedral sites as found in most chalcopyrite structures [10]. However, *n*-$CuInS_2$ chalcopyrite is known to be difficult to grow [47]. Therefore, $CuIn_5S_8$ spinel phase being typically *n*-type and having a similar band gap of 1.5 eV, matches well with the solar spectrum for energy conversion [6]. $CuIn_5S_8$ is visible-light-active materials with high-absorption coefficients, suitable band gaps, good radiation stability, and easy conversion between *n*- and *p*-type carrier types which permits a variety of potentially low-cost homo and hetero junction [5,7]. An efficiency of about 9.1% was associated with the *p*-$CuInS_2$/CuI/*n*-$CuIn_5S_8$ tandem structure solar cell [8]. A variety of physical and chemical techniques have been employed to fabricate this material [11–13]. Among these methods, electrodeposition as a cheap and facile method is widely used for the co-deposition of copper indium sulfide thin films under particular conditions [14–17]. It is easy to scale up to produce films with good quality and large area [18]. But a potential problem in the development of this technique is the control of the sample composition which is directly related to the electrodeposition conditions and concentrations.

Studies concerning the $CuIn_5S_8$ semiconductor/electrolyte interface (namely polysulfide electrolyte) have been investigated in some detail by many authors [19–22]. Even though these studies demonstrated the importance of these semiconductors as electrodes in photoelectrochemical cells, previous efforts lacked a systematic study necessary to understand the phenomena related to the $CuIn_5S_8$ semiconductor/electrolyte interface by means of electrochemical impedance spectroscopy technique (EIS). This latter technique constitutes a powerful tool for studying semiconductor/electrodes barrier, which measures the response of a sample under an AC stimulus in which the frequency is varied over a wide range. EIS has wide applicability, and has been used for the study of ionic conductors, dielectric materials, semiconductors,

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Table 1
Deposition parameters of the samples and atomic composition determined by XRF analysis.

[Cu]/[In] ratio	Bath composition (mM)				Atomic ratio obtained from XRF analysis (at%)			
	Cu^{2+}	In^{3+}	$S_2O_3^{2-}$	KCl	Cu (at%)	In (at%)	S (at%)	Cu:In:S
0.5	1	2	10	250	8.5	27.2	64.2	1:3.18:7.51
0.4	1	2.50	10	250	8.1	32.5	59.3	1:3.97:7.24
0.33	1	3	10	250	7.9	34.9	57.1	1:4.40:7.21
0.28	1	3.50	10	250	7.2	37.8	54.8	1:5.21:7.54
0.25	1	4	10	250	6.7	39.9	53.3	1:5.91:7.90
0.22	1	4.50	10	250	6.6	40.8	52.5	1:6.17:7.96

solar cells, fuel cells, batteries and corrosion [23,24]. This technique has the potential to provide information about physical and electrical properties of semiconductor materials such as, type of semiconductor, charge carriers density (N), and flat band potential (V_{fb}) [25]. The objective in electrochemical impedance spectroscopy is to correlate features of impedance spectra with their underlying micro-structural origins by means of appropriate and reasonable equivalent circuit.

All these considerations explain our interest for studying the electrochemistry of $CuIn_5S_8$ films by EIS. The aim of this paper is to investigate the effect of [Cu]/[In] ratio in the electroplating solution on the structural, morphological and stability of the one-step potentiostatically deposited $CuIn_5S_8$ thin film onto conductive and transparent indium tin oxide (ITO)-coated glass substrates from an acidic solution. These fundamental investigations are aiming at the clarification of electrochemical behavior and physical phenomena taking place at the $CuIn_5S_8$ electrode/Na_2SO_4 electrolyte solution interface utilizing electrochemical impedance spectroscopy.

2. Experimental

2.1. Materials preparation

The electrodeposition has been carried out potentiostatically using an Autolab potentiostat/galvanostat PGSTAT 30 (Eco Chemie BV) connected to a three-electrode cell (K0269A Faraday Cage, Par). The working electrode was (ITO)-coated glass substrate (average area = 1 cm^2, $\rho \leq 5.0 \times 10^{-5}\ \Omega$ cm), the reference electrode was an Ag/AgCl (3 M NaCl) and a platinum plate was used as counter electrode. Before using, all (ITO)-coated glass substrates were ultrasonically cleaned during 15 min with acetone and isopropanol, respectively and rinsed with deionized water and finally dried in air at room temperature. The copper to indium molar ratio [Cu]/[In] in precursor solution was varied during the deposition of samples. The solution baths, which were well stirred, contained 1 mM $CuCl_2$, (Sigma–Aldrich, 97%) for copper, 2–4.5 mM $InCl_3$, (Sigma–Aldrich, 98%) for the indium and 10 mM $Na_2S_2O_3$ $5H_2O$, (Fluka, ≥99%) (check Table 1). All the precursors were dissolved in deionized water with 0.25 M KCl as the supporting electrolyte. The pH of the solution was adjusted to 3.0 by adding drops of concentrated 1.0 M HCl in order to decrease the formation of metal complexes such as $In(OH)_3$. The uniform and well adherent $CuIn_5S_8$ spinel thin films were deposited at optimized deposition potential of −1.0 V (vs. Ag/AgCl). Details of the deposition process are reported in a recent past work [17]. The deposition time (t_d) was kept at 15 min with magnetically stirring [4]. The obtained samples have been rinsed with deionized water and then dried in air at a room temperature. Due to the amorphous nature of as-deposited films and in order to improve their crystallinity, all as-deposited films have been annealed in N_2 atmosphere at 350 °C for 60 min. The detailed analysis of thermal treatments on the crystal structure of $CuIn_5S_8$ thin films has been investigated in past work [5].

2.2. Characterizations

The crystal phase of the films was analyzed using an X-ray diffractometer (automated Bruker D8 advance) with CuKα (λ = 1.541 Å) radiations in the 2θ range of 10–70°. The obtained structural data were examined with X'Pert HighScore Plus program. The morphology of samples was analyzed using a scanning electron microscope (SEM, JEOL JSM-6700), with an accelerating voltage of 15 kV. The impact of the precursor's molar ratio onto the composition of samples was estimated by X-ray fluorescence (XRF) using a spectrometer MagiX PW2403.

2.3. Electrochemical measurements

The measurement of electrochemical impedance investigations and Mott–Schottky plots were carried out using a computer-controlled potentiostat (PGSTAT 30) equipped with a frequency response analyzer and connected to a three-electrode cell (as described above). The surface area of the working electrode is about 0.5 cm^2. All electrochemical measurements were released in an electrolyte solution of 0.5 M Na_2SO_4 (pH 6.5) [26]. EIS measurements were carried out at the open-circuit potential. A

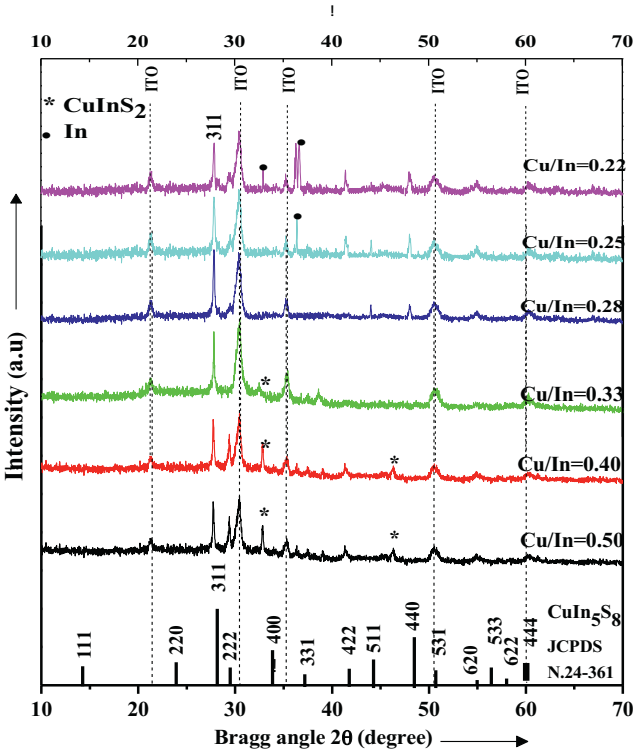

Fig. 1. XRD patterns of electrodeposited $CuIn_5S_8$ thin films onto ITO-(glass) substrate prepared from mixing precursor with [Cu]/[In] ratios between 0.22 and 0.5.