Materials Science in Semiconductor Processing 16 (2013) 1665–1671

Contents lists available at SciVerse ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Pulse electrodeposited copper indium sulpho selenide films and their properties

A. Shanmugavel [a,b], K. Srinivasan [c], K.R. Murali [d,*]

[a] Research and Development Centre, Bharathiar University, Coimbatore 641046 India
[b] Department of Physics, Kanchi Pallavan Engineering College, Kancheepuram, India
[c] Department of Physics, Government Engineering College, Salem, India
[d] ECMS Division, CSIR-CECRI, Karaikudi 630006, India

ARTICLE INFO

Keywords:
I–III–VI2
Thin films
Semiconductors
Electronic materials

ABSTRACT

Copper indium sulpho selenide films of different composition were deposited by the pulse plating technique at 50% duty cycle (15 s ON and 15 s OFF). X-ray diffraction studies indicated the formation of single phase chalcopyrite copper indium sulpho selenide films. Transmission Electron Microscope studies indicated that the grain size increased from 10 nm–40 nm as the selenium content increased. The band gap of the films was in the range of 0.95 eV–1.44 eV. Room temperature resistivity of the films is in the range of 16.0 Ω cm–33.0 Ω cm. Films of different composition used in photoelectrochemical cells have exhibited photo output. Films of composition, $CuInS_{0.9}Se_{0.1}$ have exhibited maximum output, a V_{OC} of 0.74 V, J_{SC} of 18.50 mA cm^{-2}, *ff* of 0.75 and efficiency of 11.40% for 60 mW cm^{-2} illumination.

1. Introduction

$CuIn(S,Se)_2$ abbreviated as (CISS) is an interesting material for the fabrication of thin film solar cells due to its high absorption coefficient, suitable band gap and good stability. To fabricate CISS based heterojunction thin film, solar cell is a recent research and development area for obtaining higher efficiency solar cells. All the thin film deposition techniques used for the fabrication of high efficiency (CISS) compound based cells are very expensive and require sophisticated instruments. In some deposition techniques, H_2Se and H_2S vapours are used as source materials for selenium and sulphur, which are poisonous gases. A number of thin film growth technologies such as sulphurisation and selenization [1], two step growth [2], co-sputtering and thermal diffusion [3] and one-step electrodeposition [4], chemical bath deposition [5] have been investigated for the synthesis of CISS thin film compounds. In this work, the pulse electrodeposition technique has been employed for the first time to prepare CISS films. In this paper, properties of CISS films deposited by pulse electrodeposition are presented and discussed.

2. Experimental methods

CISS films were deposited on tin oxide coated glass substrates (5 Ω/sq) and titanium substrates at 80 °C at 50% duty cycle. The precursor solution was 0.1 M $CuCl_2$, 0.1 M $InCl_3$ and the concentration of sodium thiosulphate and SeO_2 was varied to get different composition of CISS films (Table 1). The deposition potential was fixed at −0.90 V vs. saturated calomel electrode (SCE). The total deposition time was 60 min in all cases. Cyclic voltammetry (CV) was recorded using EG &G 362 scanning galvanostat/potentiostat.

CV was recorded to understand the codeposition procedure of Cu, In, S and Se. Fig. 1 shows the CV recorded for

* Corresponding author. Tel.: +91 4565 227550; fax: +91 4565227553.
E-mail address: muraliramkrish@gmail.com (K.R. Murali).

1369-8001/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.mssp.2013.05.002

Table 1
Concentration of sodium thiosulphate and selenium dioxide for obtaining CISS films of different composition.

Concentration of $Na_2S_2O_3$ (M)	Concentration of SeO_2 (M)
0.025	0.225
0.050	0.200
0.075	0.175
0.100	0.150
0.125	0.125
0.150	0.100
0.175	0.075
0.200	0.050
0.225	0.025

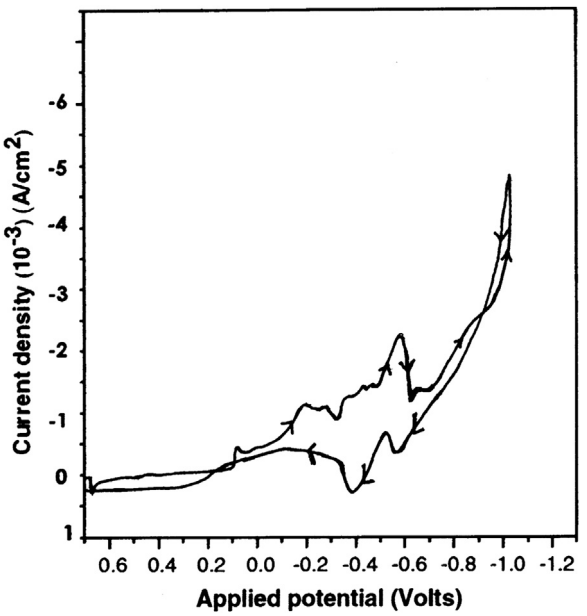

Fig. 1. Cyclic voltammogram of obtained in a mixture of Cu, In,S and Se in the electrolytic bath.

CISS bath on tin oxide working electrode. The features related to the deposition of CISS were observed. Initially, at lower cathodic potential up to −0.4 V, the features noticed were related to the reduction of Cu, S and Se by charge-transfer reaction

$$Cu^{2+}+2e^{-}\rightarrow Cu\ (s);\ E_0=0.34\ V\ (NHE) \quad (1)$$

$$HSeO_2^{+}+4e^{-}+3H^{+}\rightarrow Se\ (s)+3H_2O;\ E_0=0.74\ V\ (NHE) \quad (2)$$

$$HSO_3^{+}+5H^{+}+4e^{-}\rightarrow S\ (s)+3H_2O;\ E_0=0.420\ V\ (NHE) \quad (3)$$

The deposition of indium was observed beyond the potential −0.6 V with respect to SCE reference electrode, by following charge-transfer reaction

$$In^{3+}+3e^{-}\rightarrow In(s);\ E_0=-0{:}34\ V\ (NHE) \quad (4)$$

A cross over at −0.9 V favors the nucleation and deposition of CISS alloys. Sharp linear rise in cathodic current observed beyond −0.9 V could be due to the hydrogen evolution. During anodic curve, the dissolution (stripping) peaks for In, Cu, S and Se were observed. Thickness of the films measured by Mitutoyo surface profilometer increased from 0.4–0.7 μm with increase of selenium concentration. The films were characterised by X-ray diffraction (XRD) technique to study the structural characteristics using a Philips X-ray diffractometer and with CuKα radiation. Surface morphology of the films was studied by molecular imaging atomic force microscope and also by a Transmission Electron Microscope (TEM) (JEM 2000FX). TEM sample preparation for the observation of nanostructured thin films was done by the following procedures: the film was scraped off from the tin oxide glass with a spatula into an agate mortar. Then the finely milled oxide powder was dispersed in 1:1 mixed solution of water and alcohol for an hour. A small amount of the liquid taken from the above solution was dropped on the microgrid of each TEM sample holder, which was then dried. Optical transmission spectra were recorded using U 3400 UV–vis-NIR spectrophotometer. Electrical properties were studied by evaporating Indium ohmic contacts on the sides of the top surface of the films. X-ray photoelectron spectroscopy (XPS) spectra were recorded using VG MKII spectrometer with MgKα radiation. Photoelectrochemical (PEC) cell studies were made in 1 M polysulphide electrolyte (1 M each of NaOH, Na_2S and S) using a 250 W tungsten halogen lamp.

3. Results and discussion

Fig. 2 exhibits the X-ray diffraction (XRD) spectra of three representative $CuInS_xSe_{1-x}$ films of different composition. All the peaks observed in the films were corresponding to the diffraction lines from $CuIn(S_xSe_{1-x})_2$ and no peaks were found from $Cu_{2-x}Se$ or Cu_2Se or In_2S_3–In_2Se_3 phases. All of the thin films were strongly oriented to the (112) plane. Peaks corresponding to the (112),(200/004),(220/204) planes of the chalcopyrite phase was observed in all cases (JCPDS 36-1311). All these peaks shift to higher angle with increasing the sulphur content in the film. The lattice parameters, '*a*' and '*c*' were calculated from the diffraction spectra using the built in software. The lattice parameters '*a*' and '*c*', decrease with increase in sulphur content, since as the sulphur concentration increases, the lattice parameters shift from copper indium selenide side to copper indium sulphide side. The peaks shifted to higher angle side with increase of sulphur content. Similar observations were observed earlier [6]. Fig. 3 shows the variation of '*a*' and '*c*' with increase of sulphur content. The value of c/a in $CuIn(S_xSe_{1-x})_2$ thin films increases linearly from 2.006 to 2.018 with increasing '*x*' from 0 to 1.0.

The crystallite size was calculated using the Scherrer's equation

$$\text{Crystallite size}(D)=0.9\lambda/\beta\ \cos\theta \quad (5)$$

where, λ is the wavelength of X-ray (CuKα radiation), β is the full width at half maximum (FWHM) of the X-ray diffraction peak. The values of crystallite size and thickness