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Effect of Current Densities on Structural and Optical Properties of Brush Plated CuInSe₂ (CIS) Thin films

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Abstract

CuInSe (CIS)-based thin film compounds are considered one of the most efficient absorber materials for solar cell applications, now reaching conversion efficiencies as high as almost 20% for laboratory-sized devices. To make CIS-based thin films solar cells even more attractive and competitive, an alternative low cost process has to be developed for the manufacture of the high quality CIS absorber layers. In this work, CIS films were deposited by the brush plating technique for the first time. AR grade Copper sulphate (0.03M), Indium sulphate (0.05 M) and 0.005 M Selenium oxide was used for the deposition of films. The deposition current density was varied in the range of 10 – 100 mA cm⁻². XRD analysis of the as-deposited films verified the existence of the main Bragg peaks for CIS in a chalcopyrite crystal structure. The chemical composition of the films identified using XPS found to be copper rich. Tauc's plot indicated a direct band gap of 0.99 eV. Surface morphology of the films indicated an increase of grain size and RMS value of surface roughness from 0.32 to 1.3 nm with deposition current density. Raman spectra of the films exhibited an intense peak at around 175 cm⁻¹. This peak can be assigned to the A₁ mode of CIS. Photoelectrochemical cell (PEC) studies indicated an open circuit voltage of 0.49V and short circuit current density of 13 mA cm⁻² for the films deposited at 100 mA cm⁻². The photo output increased with deposition current density.

Keywords: Thinfilms; Chalcopyrite; Energy bandgap.

1. INTRODUCTION

In recent years, there has been a growing attention to ternary chalcopyrite compound CuInSe₂ (CIS) and its alloys with gallium CuIn_xGa_{1-x}Se₂ (CIGS) owing to their promising performance for thin film solar cell applications. The conversion efficiencies have already exceeded 19% using these materials at the laboratory scale (Repins et al. 2008). Up to now, there are a large variety of approaches to be employed for CIS-based absorber layer

fabrication, such as co-evaporation (McCandless et al. 1988), RF sputtering (Abdul-Hussein et al. 1985), molecular beam epitaxy (White et al. 1979), metal organic chemical vapor deposition (Yoon et al. 2006), spray pyrolysis (Akl et al. 2008) and electrodeposition (Guillemoles et al. 1994). Amongst them, electrodeposition is an appealing technique that offers low-cost equipment, efficient material utilization and scalability for large area thin films deposition. Over the past decades, CIS thin films have been successfully electrodeposited using direct current (d.c.) under the potentialstatic or galvanostatic condition (Ramdani et al. 2007) and periodic pulse electrodeposition technique

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(Endo et al. 1996). In this work, the brush plating technique has been employed for the first time to deposit CIS films.

2. EXPERIMENTAL

CIS films were deposited by the brush plating technique for the first time. AR grade Copper sulphate (0.03M), Indium sulphate (0.05 M) and 0.005 M Selenium oxide was used for the deposition of films. The deposition current density was varied in the range of 10 – 100 mA cm⁻². The deposition was done on Indium tin oxide substrates at room temperature. Thickness of the films estimated by Mitutoyo surface profilometer increased from 400 nm to 800 nm. The films were characterized by X-ray diffraction using Philips x-ray unit and CuK α radiation. Optical studies were made with U3400 UV-VIS-NIR spectrophotometer. Composition of the films were measured using XPS attachment. Surface morphology of the films was measured with Molecular Imaging Atomic force microscope. Photoelectrochemical cell studies were made with ORIEL 250 W Tungsten halogen lamp. Raman spectrum was recorded using Renishaw Invia Microscope attached with a 633 nm He-Ne laser.

An electroplating process performed with hand held portable tool rather than a tank of solution is known as brush plating. The brush plating processes are also called as contact plating, selective plating or swab plating. This is essentially a plating method, deposition of a metal on the surface by electrochemical means, where the work is connected cathodically to the current source. The plating is then applied by means of a brush or swab, soaked with solution and connected to a flexible anode cable. A direct current power pack drives the electrochemical reaction, depositing the desired metal on the surface of the substrate. In practice, movement between the anode and cathode is required for optimum results when plating, stripping, activating and so on. Currently a broad range of metals can be plated by brush plating. The key advantage of selective plating is portability. Many systems can be moved to various locations in a As

production facility or be transported to the job site. Selective plating is also versatile since it permits most electroplate types to be deposited onto any conductive substrate that can be touched with an electrode. Cast iron, copper, stainless steel and aluminium can be plated by this method and exhibit good adhesion. Limited adhesion can be obtained with other materials such as titanium, tungsten and tantalum.

Brush plating allows higher current densities than tank plating, which translates into higher deposition rates, upto 0.01 mm/min. In addition, inherently precise thickness control permits plate buildup or repair without the need for subsequent machining.

3. RESULTS AND DISCUSSION

The typical XRD patterns of CuInSe₂(CIS) films deposited at different current densities exhibit the chalcopyrite structure which is easily identified for the films (JCPDS card no. 00-040-1487). The films deposited at current densities less than 10 mA cm⁻², show a poor crystallinity with weak and broadened diffraction peaks as shown in fig.1

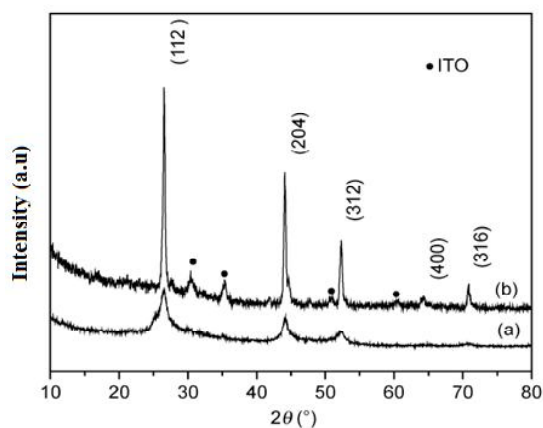


Fig. 1: X-ray diffraction patterns of CuInSe₂ films deposited at different deposition current densities (a) 10 mA cm⁻² (b) 100 mA cm⁻²

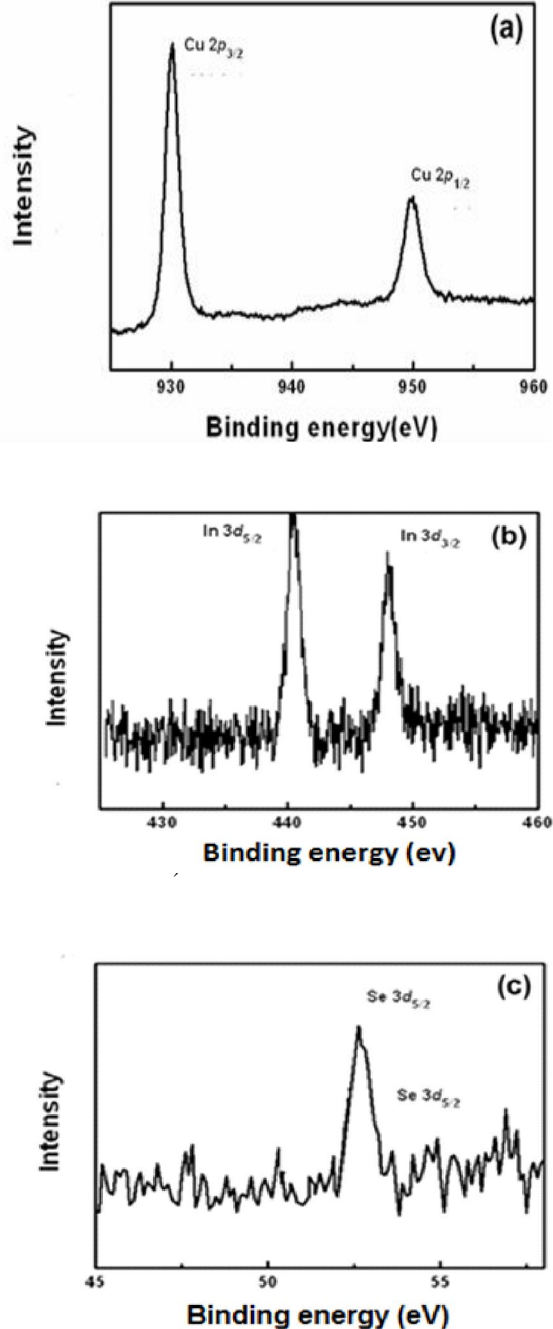


Fig.2 - XPS spectra of CIS films deposited at 100 mA cm⁻²

the deposition current density increases, the diffraction peaks become sharp and the peak intensity is also greatly enhanced. Three well defined characteristic peaks at 26.6°, 44.1° and 52.4° corresponding to the diffraction of the (112), (204) and (312) planes, respectively. Grain size estimated from Scherrer's equation which is increased from 15 nm – 40 nm with increase of deposition current density.

XPS analysis was performed to identify the chemical binding states of the constituents of the CuInSe₂ films deposited at a substrate temperature. Fig.2a represents the Cu 2p core level spectrum. The observed peak located at 931.6 eV coincides with the binding energy for Cu 2p_{3/2} electrons emitted from CuInSe₂ compound (Briggs et al 1993) and the peak at 951 eV corresponds to the binding energy for Cu 2p_{1/2} electrons emitted from Cu element (Wagner et al 1978). Fig. 2b shows the In 3d core level spectrum. The observed binding energy peaks located at 441.2 eV and 448.3 eV are attributed to the electronic state of In 3d_{5/2} and In 3d_{3/2}. As shown in Fig. 2c, there are two peaks for the Se 3d core level spectrum. The peak at 53.6 eV corresponds to the electronic state of Se 3d_{5/2} from the CuInSe₂ compound (Wagner et al 1978) and the peak at 54.9 eV coincides with Se 3d_{3/2} from the Se element (Wagner et 1978).

Three dimensional Atomic force images are shown in Fig.3. With the increment of the deposition current density, the amount of island grains increases significantly. In other words, the microstructure of CIS films becomes stable gradually. It can be seen from Fig.3(c) that at 100 mA cm⁻² current density the film surface has been quite smooth and compact. This should be ascribed to the growth transformation from three-dimension mode to two dimension one, which makes for the optimization of the structure of the films. The RMS value of surface roughness increases from 0.32 to 1.3 nm with deposition current density.

Optical measurement shows that the sample film exhibits a high absorption coefficient

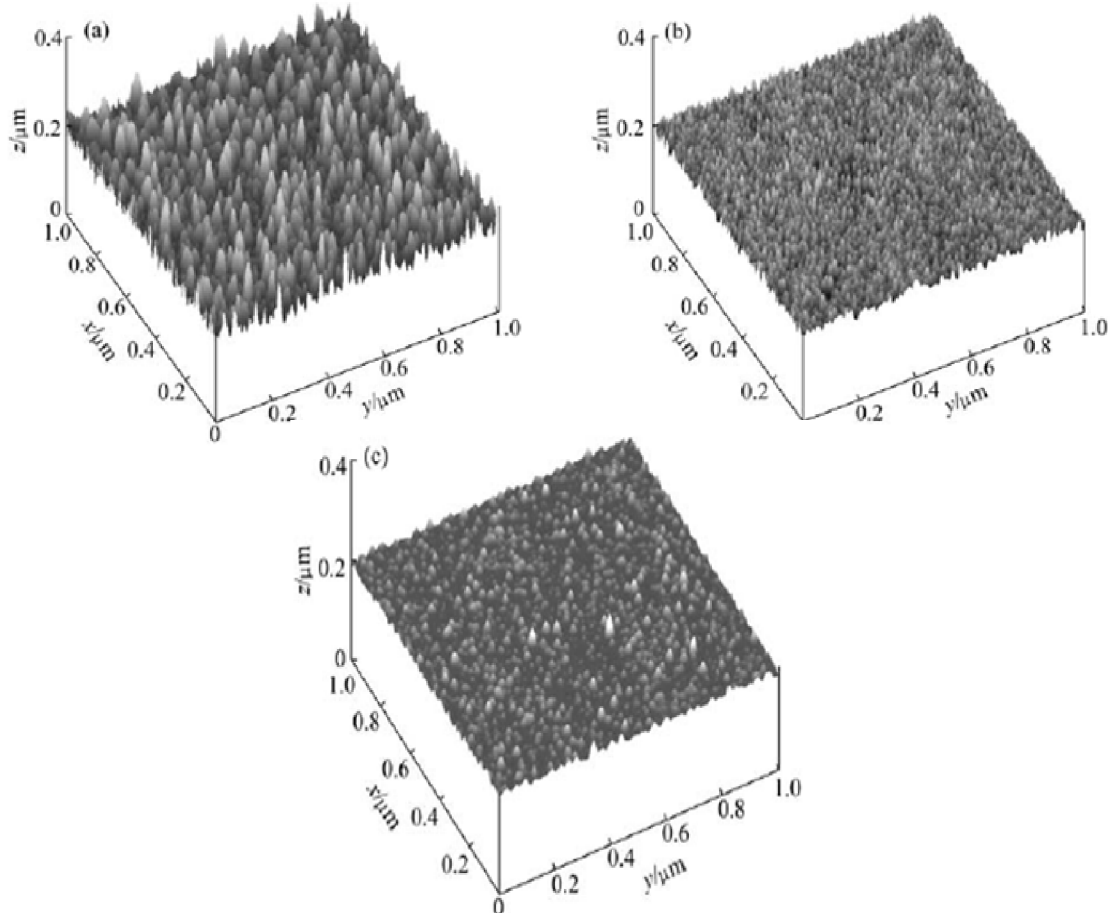


Fig.3 – Atomic force micrographs of CIS films deposited at different current densities (a)10 mA cm⁻² (b) 50 mA cm⁻² (c) 100 mA cm⁻²

of around 10^5 cm^{-1} near the fundamental absorption edge, which approaches the value for CIS films obtained by vacuum deposition. Fig. 4 shows the Tauc's plot for the films deposited at 10 mA cm^{-2} .

The energy band gap, E_g , calculated by the extrapolation of the $h\nu$ axis from the linear fit of the plot, is approximately 0.99 eV, which is similar to those reported in the literature (Kang et al 2006).

The comparison of Raman spectra of CIS films deposited at 10 mA cm^{-2} , 50 mA cm^{-2} and 100 mA cm^{-2} . The main peak is observed around 175 cm^{-1} , and could be identified as the A1 vibrational

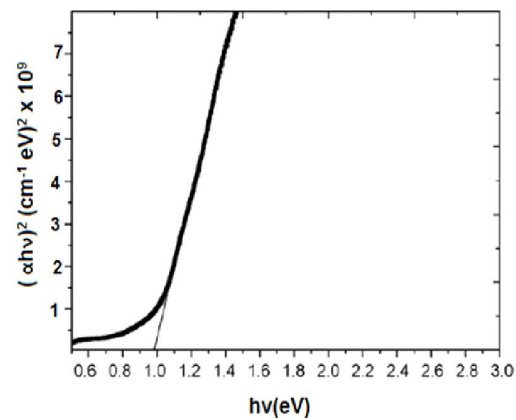


Fig.4 – Tauc's plot for CIS films deposited at 100 mA cm⁻²

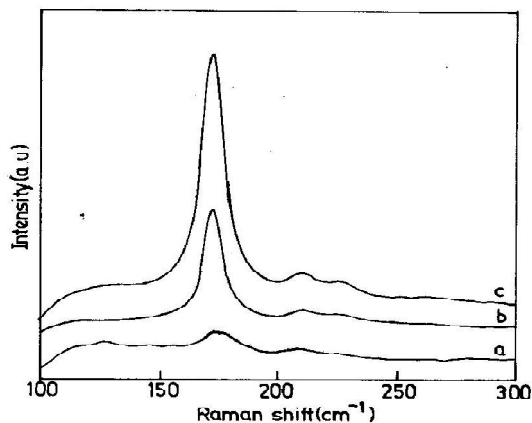


Fig.5 – Raman spectra of CIS films deposited at different current densities (a) 10 mA cm⁻² (b) 50 mA cm⁻² (c) 100 mA cm⁻²

mode from I–III–VI₂ chalcopyrite compounds (Tanino et al 1992). The slight peak shift is likely due to the extended defects such as dislocation, twins or grain boundaries at the nanocrystals because even point defects can result in changes in the Raman peak (Merdes et al 2008). It is further observed that the intensity of the major peak at 175 cm⁻¹ increases with the increase of deposition current density. A broad and weak A1 peak is observed for the films deposited at 10 mA cm⁻².

Two peaks centered at 210 and 228 cm⁻¹ are also observed in the Raman spectra for the films deposited at higher current densities. These two peaks are in good agreement with the predicted modes in CIS thin film (Rincon et al 1992).

The CIS photoelectrodes were dipped in the electrolyte and allowed to attain equilibrium under dark conditions for about 10 minutes. The dark current and voltage values were noted. The cells were then illuminated by the light source, the current and voltage were measured for each setting of the Load resistance. The photocurrent and photovoltage were calculated as the difference between the current under illumination and the dark

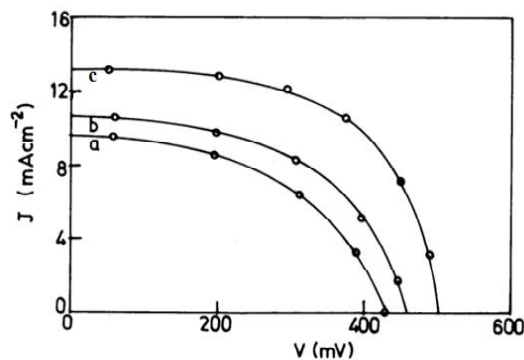


Fig.6 – Load characteristics of CIS films deposited at different current densities (a) 10 mA cm⁻² (b) 50 mA cm⁻² (c) 100 mA cm⁻²

current, and voltage under illumination and dark voltage.

The power output characteristics of the photoelectron chemical cells (PEC) made using the photoelectrodes deposited at different current densities is shown in Fig.6.

From the figure, it is observed that the PEC output parameters, viz., open circuit voltage and short circuit current were found to increase with deposition current density. For the films deposited at 100 mA cm⁻², V_{oc} of 0.49V, J_{sc} of 13 mA cm⁻², ff of 0.72 and efficiency of 7.67% for an illumination of 60 mW cm⁻².

CONCLUSIONS

Chalcopyrite structure of CIS films with band gap of 0.99 eV. The grain size in the range of 15 – 40 nm can be deposited by the brush plating technique.

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