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Towards sustainable materials for solar energy conversion: Preparation and photoelectrochemical characterization of Cu_2ZnSnS_4

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Abstract

The feasibility of a new fabrication route for films of the attractive solar absorber Cu_2ZnSnS_4 (CZTS) has been studied, consisting of electrodeposition of metallic precursors followed by annealing in sulfur vapour. Photoelectrochemical measurements using a Eu^{3+} contact have been used to establish that the polycrystalline CZTS films are p-type with doping densities in the range $(0.5–5) \times 10^{16}\ cm^{-3}$ and band gaps of 1.49 ± 0.01 eV, making them suitable for terrestrial solar energy conversion. It has been shown that a somewhat Cu-poor composition favours good optoelectronic properties.

Keywords: Photoelectrochemistry; Photovoltaics; Cu_2ZnSnS_4; CZTS; Solar cell; Semiconductor

1. Introduction

Cu_2ZnSnS_4 (CZTS) is a p-type semiconductor that has received little attention in the literature. In contrast to well known solar absorber materials such as $Cu(In,Ga)(S,Se)_2$ (CIGS) and CdTe, CZTS contains only abundant, non-toxic elements. CZTS is reported to have a band gap between 1.45 and 1.6 eV [1–3] (in the optimum range for a single junction solar cell [4]) and a band edge absorption coefficient above $10^4\ cm^{-1}$ [5]. Katagiri and co-workers [1,5,6] have prepared 5.7% efficient CZTS cells by a vacuum sputtering process followed by annealing in H_2S [1].

Electrodeposition of precursor layers followed by thermal annealing has been used to fabricate CdTe solar cells (the BP Apollo® process [7]) and also CIGS cells (the CISEL project [8]). The objective of the present work was to develop an electrochemical approach to fabricate CZTS absorber films, and to use photoelectrochemical techniques to investigate the (largely unknown) material properties of CZTS without the need to build complete solar cells. CZTS films were formed by sequential electrodeposition of the constituent metals followed by annealing in sulfur vapour. Photoelectrochemical characterization of the films was performed using transparent electrolyte contacts containing the $Eu^{3+/2+}$ redox couple [9].

2. Experimental

Soda-lime glass substrates (25 × 10 mm) coated with a 1 μm sputtered molybdenum layer were cleaned ultrasonically in detergent, distilled water, ethanol and isopropanol and dried under flowing nitrogen. A 10 × 10 mm deposition area was masked off with PTFE tape. Cu, Sn and Zn layers were deposited sequentially at room temperature without stirring in separate 3-electrode cells with platinum counter and Ag|AgCl reference electrodes using an Autolab 20 potentiostat. Solutions were prepared using milliQ water and salts of 4N purity or higher. Deposition solutions and conditions were as follows: Cu – 1.5 M NaOH, 0.1 M

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Sorbitol, 50 mM $CuCl_2$, −1.14 V [10]; Sn – 2.25 M NaOH, 0.45 M Sorbitol, 55 mM $SnCl_2$, −1.21 V [11]; Zn – pH 3 Hydrion buffer, 0.15 M $ZnCl_2$, −1.20 V.

The layered metal films and a 100-fold excess of sulfur (5 N, Alfa Aesar) were loaded into a graphite container, which was inserted into a tube furnace. After drying at 100 °C under vacuum, the tube was filled with argon to 1 bar and heated at a rate of 40 °C min^{-1} to 550 °C, which was maintained for 2 h. The system was then purged with nitrogen and allowed to cool naturally.

Photoelectrochemical measurements were carried out in 3-electrode mode in 0.2 M $Eu(NO_3)_3$ with platinum wire counter and Ag|AgCl reference electrodes. Samples were illuminated with monochromatic light of variable wavelength chopped at 27 Hz. A lock-in amplifier (Stanford Research Systems) was used to measure the photocurrent. The system was calibrated using a standardized silicon photodiode. Film morphology was examined using a JEOL JSM6310 scanning electron microscope. X-ray diffraction measurements were carried out with a Philips PW1820/00 diffractometer. Film compositions were determined by energy dispersive X-ray spectroscopy (EDS) and by atomic absorption spectroscopy (AAS) analysis of films dissolved in nitric acid.

3. Results and discussion

CZTS samples (designated A–D) with a nominal thickness of 1 μm were prepared with coulometrically controlled atomic ratios Cu/(Sn + Zn) and constant Zn/Sn ratios. Previous work suggests that a slightly Zn-rich and Cu-poor composition gives good optoelectronic properties [12,13]. Fig. 1 illustrates the stages of precursor preparation. A mirror-bright, fine-grained Cu deposit is produced, followed by an island-like Sn layer with incomplete surface coverage. The final Zn layer covers the surface completely.

After sulfidation, the films appear rough and dark grey. The SEM images of Fig. 2a and b show polycrystalline films of about 1 μm thickness with grain sizes in the range 0.2–0.5 μm. Compositional analysis by AAS confirmed that the films were overall Zn-rich (Zn/Sn > 1), however EDS showed that the films were Zn-poor at the centre and Zn-rich at the edges. The Cu/(Zn + Sn) ratio was found to vary as expected between the four samples, as detailed in Table 1.

The X-ray diffraction pattern, Fig. 2c, matches literature data for CZTS (JCPDS 26-0575). Binary sulfides may also be formed, but there is no evidence for Cu_xS and only limited evidence for SnS_2. ZnS (sphalerite) is difficult to distinguish since it has only a small lattice mismatch with CZTS [14].

The samples all showed a p-type photocurrent response. Fig. 3 compares external quantum efficiency (EQE) spectra for samples A–D. The pronounced Urbach tails above 850 nm suggest the presence of sub-gap states near the band edge. It can be seen that the optimum Cu/(Zn + Sn) ratio is around 0.9. In agreement with previous work [12], Cu-rich films performed poorly. The steady increase in EQE below the onset wavelength indicates a high acceptor density, combined with a low electron diffusion length. The high acceptor density corresponds to a space charge layer

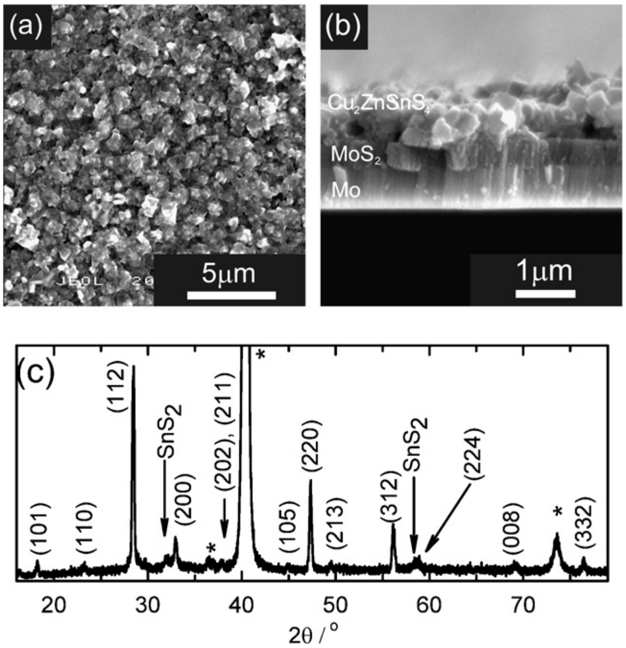

Fig. 2. SEM images of Cu_2ZnSnS_4 film showing (a) surface of sample B, and (b) edge of sample C. (c) X-ray diffraction pattern of Cu_2ZnSnS_4 film. Peaks marked (*) arise from the substrate.

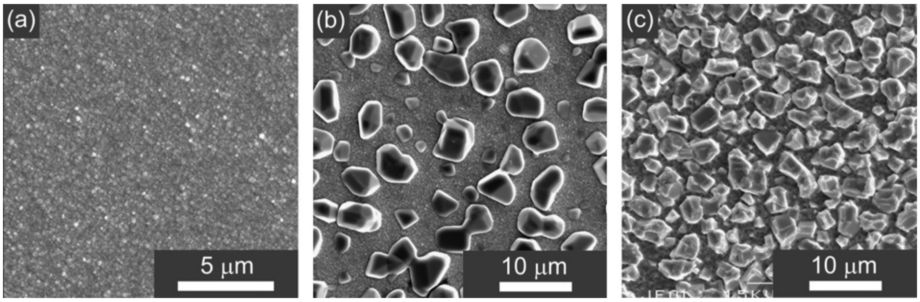

Fig. 1. SEM images of precursor metal layers (a) Cu, (b) Sn, (c) Zn.