Towards Sustainable Photovoltaic Solar Energy Conversion: Studies Of New Absorber Materials

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The implementation of terawatt photovoltaic solar energy conversion will place new demands on materials supply and environmental impact. As a consequence, the search for sustainable photovoltaic materials that combine low cost with low toxicity and low energy manufacturing processes is becoming increasingly important. This paper examines the preparation and properties of two emerging indium-free photovoltaic absorber materials, Cu_2ZnSnS_4 and Cu_3BiS_3. Electrochemical routes to fabrication of absorber layers are considered, and characterization methods based on photoelectrochemistry and electrolyte contacts are discussed.

Introduction

The European Union set 2020-2030 as the target for photovoltaic (PV) generated electricity to become competitive with conventional electricity generation. The EU also agreed a binding target of a 20 % share of renewable energies in overall EU energy consumption by 2020. With the prospect of large scale deployment of terrestrial PV becoming realistic, issues of sustainability and costs of raw materials for device manufacture are assuming greater importance. It is becoming clear that there could be issues of long-term sustainability in terms of cost and availability for thin film PV technologies based on CdTe and $Cu(In,Ga)Se_2$ (CIGS). The search for alternative sustainable absorber materials, as the key component inside thin film photovoltaic devices, is therefore timely.

Two promising candidates containing only abundant non-toxic elements are being studied in our laboratory: Cu_2ZnSnS_4 (CZTS) (1-4) and, more recently, Cu_3BiS_3. CZTS can be considered as an analogue of $CuInS_2$ (CIS) obtained by replacing In(III) by Zn(II) and Sn(IV) in a 50:50 ratio. It is a p-type semiconductor with a direct bandgap in the range 1.45 – 1.6 eV (5-7). CZTS has been prepared by in-line vacuum sputtering of Cu, SnS and ZnS followed by annealing in a hydrogen sulfide atmosphere (5,8,9), and photovoltaic devices with these films have achieved AM 1.5 efficiencies of up to 6.7% (10). Cu_3BiS_3 films have been made by solid state reaction of a bismuth overlayer with a film of CuS deposited from a chemical bath (11) and by reactive sputter deposition of CuS and Bi on heated silica substrates (12). The material appears to have a direct forbidden bandgap at 1.4eV. We are unaware of any reports of photovoltaic devices fabricated with Cu_3BiS_3.

In the present work, electrodeposition was chosen as a low cost and scalable alternative to vacuum sputtering. Electrodeposition of precursor layers followed by thermal annealing has been demonstrated as a suitable method for fabricating for CdTe solar cells (13) and CIGS cells (14). Photoelectrochemical methods for characterization of absorber films have been employed in our laboratory for the characterization of CIS films prepared by an electrochemical deposition/annealing route and by sputtering (15). In the present work, electrolyte contacts containing Eu(III) as an electron (minority carrier) scavenger were used in measurements of the external quantum efficiency of the absorber film under conditions in which a Schottky barrier is formed. The results suggest that both materials should be investigated further as potential candidates for the absorber layer in heterojunction solar cells.

Experimental

Soda-lime glass substrates (25 mm x 10 mm) coated with a 1 μm radio frequency magnetron sputtered layer of molybdenum were cleaned ultrasonically in detergent, distilled water, ethanol and isopropanol and dried under flowing nitrogen. The deposition area (10 mm x 10 mm) was masked off with PTFE tape.

Cu|Sn|Zn layer stacks were deposited on the Mo substrates using a conventional 3-electrode cell with a platinum counter electrode and Ag|AgCl reference electrode. Depositions were carried out potentiostatically at room temperature (without stirring) using an Autolab 20 potentiostat. Solutions were prepared using milliQ water and metal salts of 4N purity or higher. The amounts of each metal deposited were controlled by monitoring the deposition charge. Bright and strongly adherent copper layers were deposited from an alkaline solution containing 1.5 M NaOH, 50 mM $CuCl_2$ and 0.1 M sorbitol[12] at -1.14 V vs. Ag|AgCl. Tin layers were then deposited on the copper film at -1.21 V vs. Ag|AgCl using an alkaline solution, which contained 2.25 M NaOH, 55 mM $SnCl_2$ and 0.1 M sorbitol. The final zinc layer was deposited at -1.20 V vs. Ag|AgCl from 0.15 M $ZnCl_2$ buffered to pH 3 using Hydrion buffer. The electroplated samples were washed in milliQ water and dried under nitrogen.

Cu|Sn|Zn stacked layers were annealed in a sulfur atmosphere using a quartz tube furnace. The metallic precursor films and an excess of sulfur (5N, Alfa Aesar) were loaded into a graphite container, which was inserted into the furnace tube. The samples were heated initially at 100 ^{o}C under vacuum to remove traces of water. The furnace tube was then backfilled with argon to a pressure of 1 bar and heated at 40 ^{o}C min^{-1} to a final temperature of 550 ^{o}C, which was maintained for two hours to allow the metals to react fully with sulfur. The tube was then purged with dry nitrogen and the samples removed after they had cooled naturally to room temperature.

Cu_3Bi alloy layers (1-2 microns thick) were deposited on the 10 x 10 mm Mo substrates from a solution containing 9 mM $Bi(NO_3)$, 30 mM $CuSO_4.xH_2O$, 2 M NaOH, 0.2 M sorbitol at -0.75 V vs. Hg|HgO The alloy layers were then annealed in S vapor at 450 – 500 °C for 30 minutes under flowing N_2.

The morphology of the metal precursor films and the CZTS films was examined using a JEOL JSM6310 scanning electron microscope (SEM). X-ray diffraction measurements were carried out with a Philips PW1820/00 diffractometer. Localized compositional analysis by energy dispersive X-ray spectroscopy (EDS) was performed in a FEI Quanta 200 environmental SEM fitted with an Oxford X-ray analyzer at selected positions across the samples. Plating efficiencies and mean film compositions were determined by dissolving the precursor or CZTS film in HNO_3 and analyzing the solutions using atomic absorption spectroscopy (AAS).

Photoelectrochemical measurements were made of the absorber layers using 0.2 M $Eu(NO_3)_3$ (pH 2.3) as an electron scavenging redox electrolyte. The photocurrent responses of the films were measured under potentiostatic control using a 3-electrode cell with platinum wire counter and Ag|AgCl reference electrodes. Transient photocurrents were generated using chopped illumination from a high intensity white light-emitting diode. Spatially-resolved photocurrent measurements of the CZTS film were made by mounting the sample and electrodes on a computer-controlled motorized X-Y stage, which was illuminated with 1 mm diameter spot of monochromic light (470 nm) chopped at 27 Hz. A Stanford 850 lock-in amplifier was used to measure the photocurrent. XY mapping was carried out by rastering the sample in millimeter steps. A similar setup was used to measure external quantum efficiency of the semiconductor films, with the incident photon flux was calibrated using standardized silicon and germanium photodiodes traceable to NBS standards

Results and Discussion

Cu_2ZnSnS_4

CZTS films were prepared by treatment of the metal precursor films in sulfur vapor using a range of Cu/(Sn+Zn) target ratios and a Zn/Sn target ratio of 1. The actual values of these ratios were determined by AAS. The CZTS layers produced were around 0.5 microns thick and appeared gray and non-reflective with some evidence of lateral non-uniformity. The films showed good adhesion to the Mo substrate. Cross-sectional SEM suggested the presence of an intermediate MoS_2 layer between the Mo substrate and the CZTS. Figure 1 shows the morphology of the annealed CZTS film that showed the best photoresponse (cf. Figure 4). It appears to consist of small but well-defined crystallites with an average grain size of less than 0.5 microns. EDS measurements showed that the Zn component varied across the films, which were generally Zn-poor at the centre and Zn-rich at the edges (this may explain the lateral non-uniformity observed visually).

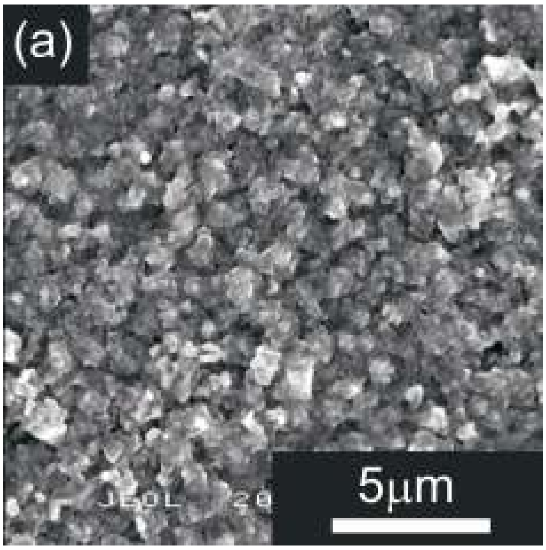

Figure 1. Top view SEM image of annealed Cu_2ZnSnS_4 film grown on molybdenum-coated glass.

Figure 2 shows the indexed XRD pattern for an annealed CZTS film. The film evidently consists primarily of CZTS, with some SnS_2. The lattice parameters (a = 0.544 nm, b = 0.542 nm, c = 1.089 nm) calculated from the X-ray diffraction pattern were matched to JCPDS card 26-0575: a = b = 0.5434 nm, c = 1.0848 nm. The XRD pattern shows no evidence of the presence of Cu_xS, but two peaks assigned to SnS_2 can be clearly seen. The ZnS content of the films is difficult to ascertain since the lattice parameters of ZnS (sphalerite) are almost identical to those for CZTS.

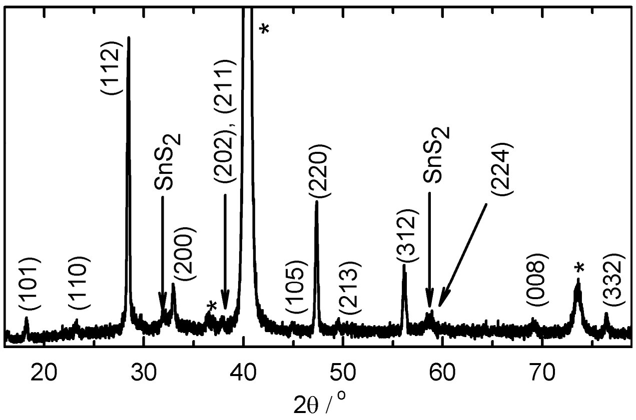

Figure 2. X-Ray diffraction pattern of Cu_2ZnSnS_4 film. The main peaks are assigned to the $CuZnSnS_4$ phase. The presence of some SnS_2 is indicated by the two labelled peaks. The unassigned peaks marked (*) arise from the molybdenum substrate.

The annealed CZTS films were characterized using a Eu(III) electrolyte to scavenge electrons reaching the surface of the illuminated semiconductor. The p-type photoactivity of the annealed films is evident from the cathodic photocurrent response seen when a flashing white LED is used to illuminate the sample during the recording of the linear scan voltammogram shown in Figure 3. The photocurrent onset is at around +0.1 V vs Ag|AgCl, and the photocurrent saturates at potentials more negative than -0.25 V. EQE spectra wer therefore recorded at a potential of -0.3 V.

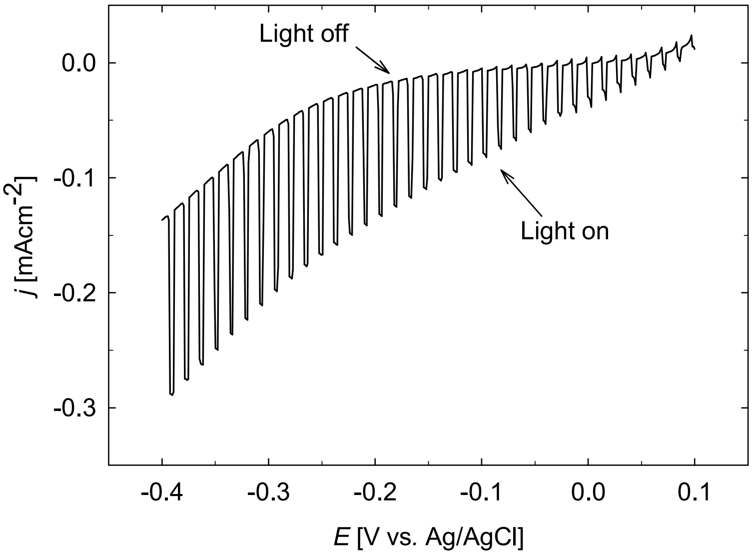

Figure 3. Voltammogram of Cu_2ZnSnS_4 film in 0.2 M Eu(III) nitrate under pulsed illumination from a white LED. The cathodic photocurrent indicates p-type behavior.

The external quantum efficiency (EQE) spectra of 4 different CZTS samples measured at -0.3V vs. Ag|AgCl in 0.2 M $Eu(NO_3)_3$ are compared in Figure 4. The highest external quantum efficiency photocurrent response is seen for sample B, which has a Cu/(Zn+Sn) ratio of 0.86 and a Zn/Sn ratio of 1.36. Sample D, which has a higher Cu/(Zn+Sn) ratio of 1.07 and a Zn/Sn ratio of 1.38 shows almost no response. Sample C, which has a Cu/(Zn+Sn) ratio of 0.91 and a Zn/Sn ratio of 1.30 is almost as good as sample B, whereas sample A, which has a Cu/(Zn+Sn) ratio of 0.71 and a Zn/Sn ratio of 1.30 gives a lower EQE.

The EQE data near the onset energy were analyzed using the relationship expected for a direct transition. The bandgap was found to be 1.49 eV, which is close to the optimum for terrestrial solar energy conversion. The shape of the EQE spectra suggests that the samples are rather highly doped and have a short electron diffusion length. Clearly it will be important to optimize the doping level and increase the minority carrier diffusion length if the material is to be used in the fabrication of efficient solar cells.

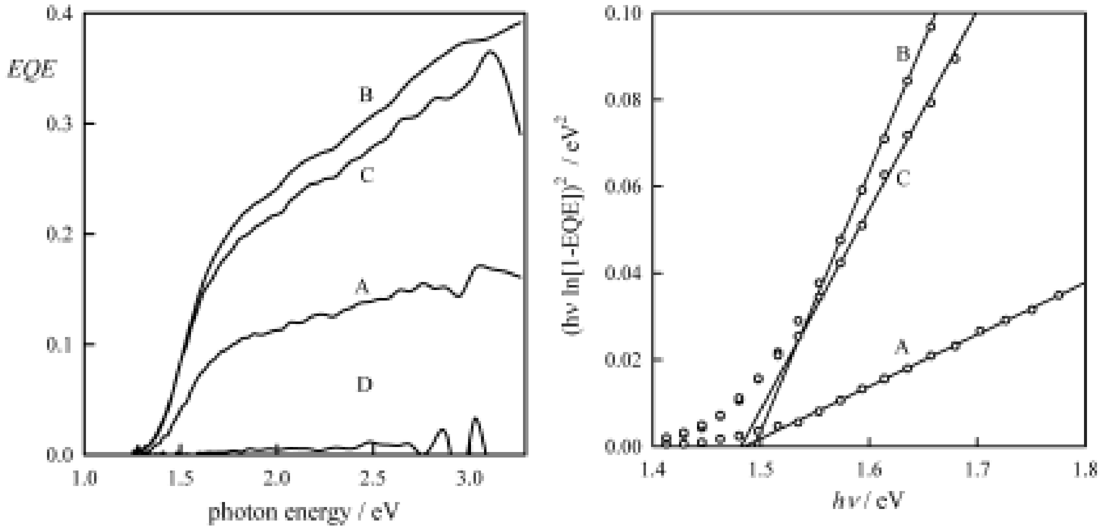

Figure 4. External quantum efficiency spectra of 4 different Cu_2ZnSnS_4 films, measured at -0.3V vs. Ag|AgCl in 0.2 M $Eu(NO_3)_3$. See text for details of stoichiometry. The plots on the right hand side were used to estimate the bandgap of the material.

The uniformity of the photocurrent response of a 2 μm CZTS film was examined using the X-Y scanning system. A typical result is shown in Figure 5. EDX analysis of similar samples shows that the highest photocurrent occurs where the ratio Cu/(Zn+Sn) is around 0.5, and the Zn/Sn ratio is greater than unity. Further work is in progress to relate the response more precisely to local variations in composition. Compositional uniformity is essential for larger area devices, and efforts are being made to achieve this by controlling mass transport during electrodeposition.

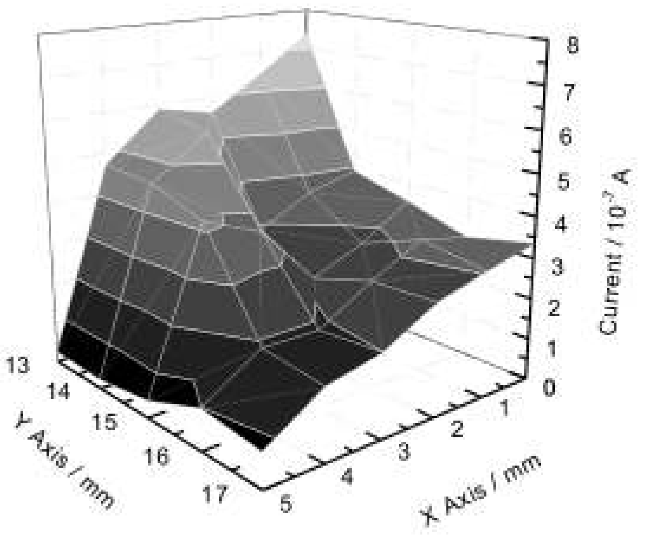

Figure 5. Spatially-resolved photocurrent response of a 2 μm thick CZTS film measured at -0.3 V vs. Ag|AgCl. Illumination wavelength 470 nm.

Fabrication of cells using CZTS has already been attempted. A thin CdS layer has been deposited on the CZTS layers using a conventional chemical bath. The cells have been completed by sputtering intrinsic ZnO followed by a layer of indium tin oxide. Results will be reported elsewhere

Cu_3BiS_3

Recently our attention has turned to Cu_3BiS_3, another potential absorber layer. Work is at an early stage, and only preliminary results are reported here. The morphology of the films produced by sulfidization of Cu-Bi alloy is illustrated by the SEM pictures in Figure 6. The film is uniform and adherent with some voids that can be seen on the cross-sectional SEM. The composition of the film is clearly very close to that expected as shown by the good match of the XRD pattern in Figure 7 to the pattern for Wittchenite.

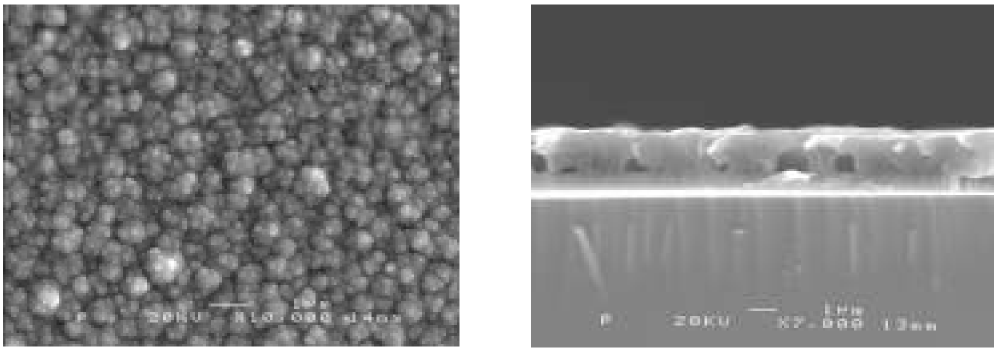

Figure 6. Top and cross-sectional SEM views of Cu_3BiS_3 film.

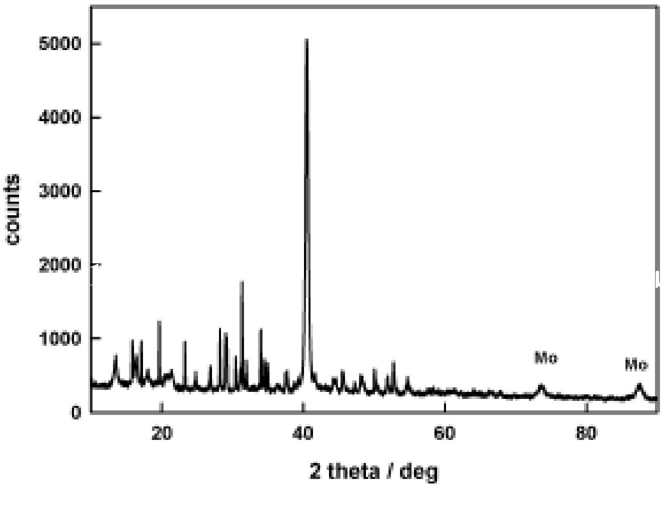

Figure 7. XRD pattern of annealed Cu_3BiS_3 film. The lines match closely with those for Wittchenite. The large central peak is from the Mo substrate

The photocurrent response of the Cu_3BiS_3 was tested using Eu(III) electrolyte. Figure 8 illustrates the response to chopped illumination from a white LED. The cathodic photocurrent response is typical for a p-type semiconductor.

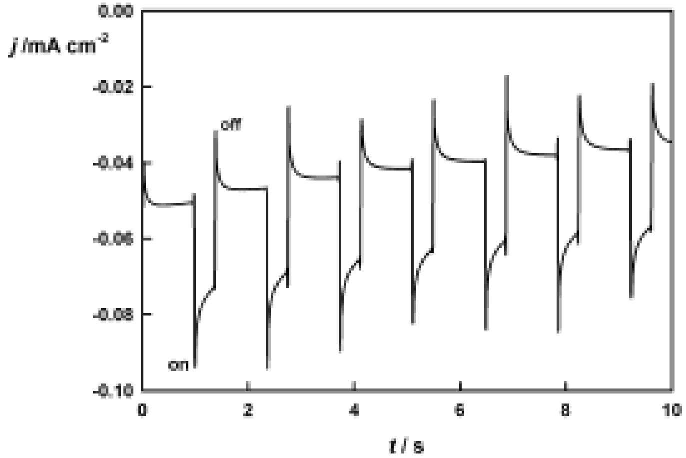

Figure 8. Transient photocurrent response measured at -0.3 V vs Ag|AgCl

The EQE spectrum of the best Cu_3BiS_3 film is shown in Figure 9. The response is smaller than that of the best CZTS film, but it is clear that the photocurrent onset wavelength is around 1000 nm, which corresponds to 1.24 eV. Work is now in progress to improve the quality of the Cu_3BiS_3 films and to enhance their photoresponse. The objective is to fabricate new solar cells using Cu_3BiS_3 as the absorber layer combined with a suitable n-type top contact.

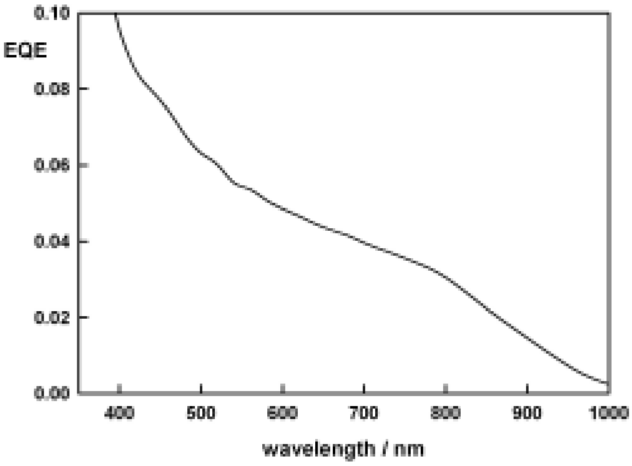

Figure 10. EQE spectrum of Cu_3BiS_3 film.

Acknowledgments

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