Thin film solar cells based on the ternary compound Cu_2SnS_3

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ABSTRACT

Alongside with Cu_2ZnSnS_4 and SnS, the p-type semiconductor Cu_2SnS_3 also consists of only Earth abundant and low-cost elements and shows comparable opto-electronic properties, with respect to Cu_2ZnSnS_4 and SnS, making it a promising candidate for photovoltaic applications of the future. In this work, the ternary compound has been produced via the annealing of an electrodeposited precursor in a sulfur and tin sulfide environment. The obtained absorber layer has been structurally investigated by X-ray diffraction and results indicate the crystal structure to be monoclinic. Its optical properties have been measured via photoluminescence, where an asymmetric peak at 0.95 eV has been found. The evaluation of the photoluminescence spectrum indicates a band gap of 0.93 eV which agrees well with the results from the external quantum efficiency. Furthermore, this semiconductor layer has been processed into a photovoltaic device with a power conversion efficiency of 0.54%, a short circuit current of 17.1 mA/cm², an open circuit voltage of 104 mV hampered by a small shunt resistance, a fill factor of 30.4%, and a maximal external quantum efficiency of just less than 60%. In addition, the potential of this Cu_2SnS_3 absorber layer for photovoltaic applications is discussed.

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1. Introduction

Research of thin film solar cells based on p-type compound semiconductor absorber layers has mainly focused on $Cu(In,Ga)(S/Se)_2$ (CIGS) and CdTe. Recently, $Cu_2ZnSn(S/Se)_4$ (CZTS) has also been considered as a possible candidate for photovoltaic applications since it only consists of abundant elements. However, potentially other p-type semiconductors with fewer elements and perhaps reduced complexity than CZTS are also available such as the ternary Cu–Sn–S system or SnS [1]. In 1987, Kuku and Fakolujo reported on the only previous device, based on a Schottky junction consisting of Cu_2SnS_3 (CTS) and indium, with a power conversion efficiency of 0.11% under 100 mW/cm² incident radiation [2,3]. Experimentally, an absorption coefficient of 10^4 cm^{-1} (at energies right above the band gap) [2–5], an electrical conductivity of $10\,\Omega^{-1}$ cm^{-1}, a hole mobility of 80 cm²/(Vs), and a hole concentration of 10^{18} cm^{-3} have been measured for a Cu_2SnS_3 phase [6]. While the absorption coefficient is in the same order of magnitude as those of CZTS and CIGS solar cells, the hole mobility and electrical conductivity measured by Avellaneda et al. for CTS seem to be a slightly higher than in the case of CZTS and CIGS thin films [6–10]. A possible explanation for these high values was given due to

the presence of $Cu_{2-x}S$ phases in those thin films. Apart from these properties, the band gap of the p-type semiconductor Cu_2SnS_3 has been reported to be between 0.93 and 1.51 eV [2–6,11,12], which lies in an optimal region for photovoltaic application. While the band gap value of 1.51 eV measured by Kuku et al. appears to be very high, values between 0.93 and 1.35 eV for the band gap seem to be dependent on the crystal structure of the polymorphic compound Cu_2SnS_3, where 0.98 eV was measured for a cubic phase and 1.35 eV for a tetragonal phase [11]. The polymorphic state of a grown Cu_2SnS_3 is dependent on the growth temperature, where the cubic Cu_2SnS_3 is known to form at high temperatures (>775 °C) and the monoclinic and triclinic as well as the tetragonal phases are low temperature phases (<775 °C) [13,14].

For this work, the samples have been prepared at temperatures where a monoclinic or triclinic phase can be expected. To prevent the sample from loosing Sn during the annealing step, which has been reported by Weber et al. [15], the samples have been annealed in a sulfur and tin sulfide containing environment since it has been shown that such an annealing method prevents CZTS layers from losing tin [16].

The focus of this work is two-fold. Firstly, we present structural, compositional, and optical properties of a monoclinic Cu_2SnS_3 thin film prepared by an electrodeposition (ED) method and a subsequent annealing, and secondly we demonstrate the fabrication of thin film solar cell devices based on this material and report its opto-electronic properties.

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2. Experimental details

The fabrication of the absorber layer was carried out in a two step process. At first, Cu and Sn were sequentially electrodeposited in a double sandwich order Mo/Cu/Sn/Cu/Sn from a basic Cu and an acidic Sn bath onto a square 25×25 mm^2 Mo-coated soda–lime glass substrate. Details of the ED method as well as the bath compositions and potentials used are given elsewhere [17]. Following the ED, the precursor was then annealed in a tube furnace at 550 °C for 2 h at 50,000 Pa (500 mbar) in a N$_2$/H$_2$ (90/10) atmosphere together with elemental sulfur (99.9995% purity) and SnS (99.5% purity) powder to convert the metal stack into the desired Cu$_2$SnS$_3$ compound. Further details of the annealing procedure can be found in [16]. The sample was etched for 30 s in a 5 wt.% KCN solution to remove the possible copper sulfide phases. Photovoltaic devices were formed by the addition of a chemical bath deposited CdS buffer layer (90 nm), followed by sputtered i-ZnO and Al:ZnO layers, and a Ni:Al front contact grid. Compositional and morphological information of the absorber layer have been gained using energy-dispersive X-ray spectroscopy (EDX: Oxford Instruments INCA X-MAX, using 20 kV acceleration voltage) and scanning electron microscopy (SEM: Hitachi SU-70), respectively, and the phase analysis has been carried out using grazing incidence X-ray diffraction (GI-XRD: Bruker D8; grazing angle of 0.75°, Cu Kα_{1+2} X-ray source). Photoluminescence (PL) measurements have been performed on a home-built setup at room temperature with an excitation wavelength of 514.5 nm using an argon ion laser, with an incident power of 40 μW, and a spot size of 1 μm^2. The PL signal has been integrated over an area of 20×20 μm^2. The solar cell devices were characterized by current density–voltage (JV) measurements using a halogen lamp (100 mW/cm^2) and the external quantum efficiency (EQE) measurement was carried out on a home-built setup. For both, experimental details can be found in Scragg et al. [17].

3. Results and discussion

3.1. Precursor

The electrodeposition conditions have been chosen in a way that the metallic layers of the precursor consist of small and densely packed grains to get uniform and homogeneously covering precursors [17]. Fig. 1(a) and (b) shows the SEM images of the metallic Cu layer on Mo and of the Sn layer on the Cu film. In both cases, a rather compact structure could be achieved, with a Cu grain size in the range of 100 nm, whereas the Sn grains reach sizes of around 600 nm. Important for the annealing, and hence for the reaction with sulfur and SnS from the gas phase, is the distribution of the metals in the precursor. We hypothesize that it is preferable for Cu and Sn to be close to each other such that a direct reaction forming Cu$_2$SnS$_3$ can be achieved. Therefore, the double sandwich stacking order has been chosen to increase the surface area between the copper and tin. It has been observed by XRD measurements (not shown here) that already at room temperature, within the first 24 h after deposition, a Cu/Sn/Cu stack alloys to form a CuSn phase. This pre-alloying supports a direct formation of the Cu$_2$SnS$_3$ phase during the process of annealing. The composition of the precursor was chosen to have a slight excess of Sn compared to stoichiometry ([Cu]/[Sn] ≈ 1.3).

3.2. Composition and morphology of the absorber layer

Unlike the metallic layers of the precursor, the morphology of the absorber layer, shown in Fig. 1(c) and (d), has a much less compact structure that is homogeneously distributed over the whole surface area of the sample. Large grains of between 2 and 6 μm in diameter can be observed with pinholes of similar horizontal dimensions. All together it was found that 67.5% of the average sample's surface is covered with grains, leaving a third with pinholes. The effect that leads to such a morphology is yet unclear, but might be connected to the annealing strategy used. The grains shown in Fig. 1(c) and (d) appear to be single phase, however an EDX compositional analysis of a single grain after KCN etching shows a Cu/Sn ratio of 1.9 and a S/(Cu + Sn) ratio of 1.09. These values are slightly S rich and Cu poor with respect to a stoichiometric Cu$_2$SnS$_3$, therefore secondary Sn rich phases cannot be excluded.

3.3. Structural investigations

Fig. 2 shows the diffractogram as obtained by GI-XRD measurements. Apart from the peaks marked with a red or green arrow, all other experimental peaks could be assigned to the monoclinic Cu$_2$SnS$_3$ phase (JCPDS: 04-010-5719, see blue vertical lines), which was discussed by Onoda et al. [13]. This phase is also the expected one at the used annealing temperature of 550 °C [13]. The marked peaks (red or green arrows) could be assigned to Mo (red) and MoS$_2$ (green). The fuzzy broad peak of MoS$_2$ at around 34° is rather dominant, which is mainly due to the large surface area of pinholes on the sample. The majority phase of this sample however can clearly be attributed to a monoclinic Cu$_2$SnS$_3$ phase.

3.4. Opto-electronic properties

3.4.1. Absorber layer

Fig. 3(a) shows a PL spectrum recorded at room temperature. There, a fairly broad and asymmetric peak at 0.95 eV can be seen, which is attributed to band–band transition, as the peak position is
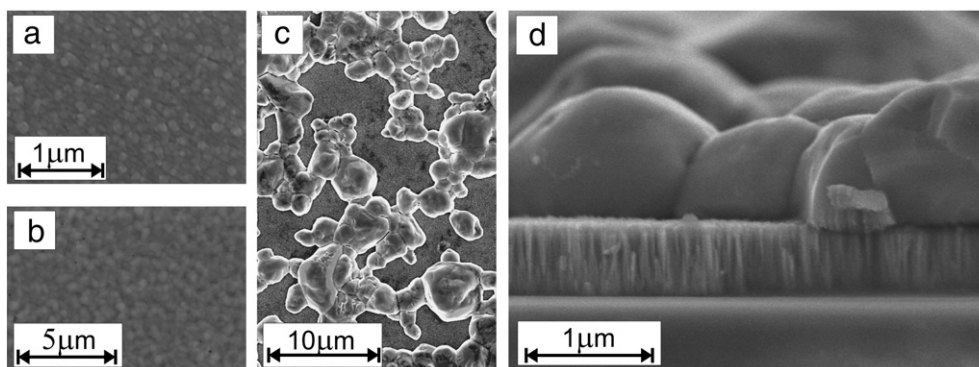

Fig. 1. SEM images of (a) the Cu layer on the Mo substrate, (b) Sn layer on Cu, (c) the etched absorber layer in top view, and (d) the etched absorber layer in cross sectional view.