**ABSTRACT**

A low-temperature colloid synthesis approach was applied to synthesize Cu₂ZnSnS₄ (CZTS) nanoparticles for the first time. This method produced gram quantities of material with a chemical yield in excess of 90% within a short synthesis time. The formation reaction of kesterite CZTS fabricated from synthesized nanoparticles was investigated, and the results showed that the sufficiently high partial pressures of Sn with S during the annealing process were important for the fabrication of high-quality CZTS films. The compositional ratios as determined by energy-dispersive X-ray spectroscopy (EDX) after the KCN etch are Cu/(Zn:Sn): 1.0 and Zn/Sn: 1.0.

Co-electrodeposition of Cu-Zn-Sn precursors for CZTS thin films was introduced for the first time by Ennaoui et al. [6]. They deposited Cu-Zn-Sn precursor layers on the Mo coated soda lime glass substrate from alkaline electrolyte bath containing Cu (II), Zn (II), and Sn (IV) metal salts in a single step. The precursor layers annealed at 550 °C in Ar-H₂S (5 %) atmosphere for 2h to allow the reaction of the precursors to form CZTS. EDX mapping analysis revealed existence of an area with reduced Sn signal near the back contact, which may point to Cu₂SnS₃ phase. Solar cells fabricated from CZTS films with Cu/(Zn + Sn) = 0.97 and Zn/Sn = 1.08 showed an efficiency of 3.4 %. Using a similar co-electrodeposition process, Araki et al. [7] reported 3.16 % efficient CZTS-based thin films solar cells. The sulfurization of the Cu-Zn-Sn precursor layers was performed at higher temperature (580 or 600 °C) compared to that reported by Ennaoui et al. (540 °C) [8] for the same time (2 h). Sample annealed at 600 °C gave the best solar cells.

1. INTRODUCTION

The successful development of chalcopyrite-type semiconductors such as Cu(In,Ga)Se₂ has led to commercialization by an increasing number of companies. Favorable optoelectronic properties yield efficiencies close to 20% on the single cell and well above 10% on the module level. Despite or even as a direct consequence of its recent and near-future success, the scarcity and increasing prices of indium eventually could limit the production growth for this type of solar cells. Seeking alternatives not containing indium, the related thin-film material Cu₂ZnSnS₄ (CZTS) shows a very similar crystal structure with a direct band gap expected in the range of 1.4–1.5 eV [1], while containing solely abundant and nontoxic elements. The elecetrodeposition of CZTSSe thin films can be summarized into two categories: sequential electropolating of precursors, and single step electrodeposition of precursors, followed by annealing under sulfur or selenium-containing atmosphere. The first report on CZTS thin films using the sequential deposition approach was who annealed a metal stack of Cu/Sn/Zn (top) deposited on a Mo coated glass substrate at 550 °C for 2 h in sulfur atmosphere. Secondary phase of SnS₂ was observed by the XRD measurement in the CZTS thin films. Devices fabricated from such films showed 0.8 % efficiencies.

Ahmed et al. [3] developed a three-step method: i) sequentially electropoleted Cu/Zn/Sn or Cu/Sn/Zn stacks; ii) annealing the stacks at low temperature (210-330 °C) under N₂ to produce homogeneous alloys; iii) annealing of these well-mixed CuZn and CuSn alloys at 550-590 °C in sulfur atmosphere for 5-15 min to allow the formation of CZTS. Secondary phases such as Cu₅S₇, SnS₂ and Cu₃SnS₄ were found in the annealed samples when the annealing temperature lowers than 580 °C. They proposed that secondary phases of ZnS and Cu₅SnS₄ reacted to form CZTS when the annealing temperature was above 580°C. Solar cells made from the CZTS samples prepared from sulfurization of CuZnSn precursors at 585°C for 12 min showed efficiencies ranging from as high as 7.3 %, which is highest efficiencies for the pure CZTS-based solar cells prepared from electrodeposition to date. Recently, Guo et al. [5] using a similar deposition process, fabricated 7.0 % efficient CZTS and CZTSe based solar cells. After annealing of the Cu/Zn/Sn metal stacks at 360 °C in N₂ for 30 min, the samples sealed in a closing quartz tube together with sulfur or selenium were annealed at 535–585 °C for 5-20 min. The optimized salination conditions were found to be at 585°C for 7 min while the optimized sulfurization conditions were at 585°C for 12 min. They proposed that the low shunt resistance in CZTSe-based solar cells (0.48 KΩ cm²) in contrast to CZTS-based solar cells (11.8 KΩ cm²) is due to the existence of a Se-poor and Sn-rich grain boundary region. They also proposed that the oxygen observed in the CZTS/CZTSe thin films may be that the sufficiently high partial pressures of Sn with S during the annealing process were important for the fabrication of high-quality CZTS films. The compositional ratios as determined by energy-dispersive X-ray spectroscopy (EDX) after the KCN etch are Cu/(Zn:Sn): 1.0 and Zn/Sn: 1.0.
that they are the optimum chalcogenide sources for the fabrication of nanoparticles in our case. It is obvious that the chalcogenide source affects the results of the synthesis reaction. The possible reason for this is the different nucleation and growth speeds caused by the different chalcogenide sources. The nucleation speed was fast and it resulted in the formation of numerous small nuclei when Na$_2$S was used. The small nuclei quickly agglomerated together by van der Waals attractive forces and grew into a big bulk, causing no nanoparticles to be detected. The slow nucleation speed caused growth of nuclei, which occurred with nucleation at the same time, resulting in the wide range of nucleus size when Na$_2$S was used as the chalcogenide source. Therefore, the size of CZTS nanoparticles, which grew from the nuclei, shows a wide distribution range. The appropriate nucleation and growth speeds with Na$_2$S were applied at the same time, resulting in a narrow distribution of diameter, and the average size of the nanoparticles was about 80 nm. The composition of the CZTS nanoparticles as-synthesized for 2 min was confirmed by Energy-dispersive X-ray spectroscopy (EDS). The yields of the CZTS nanoparticles exceeded 90%, which was determined after the evaporation treatment of the solvent. No diffraction peaks were observed in the XRD results (data not shown), suggesting that the CZTS nanoparticles were almost amorphous materials. The CZTS nanoparticles were coated on Al substrates followed by drying and partial decomposition on a preheated hot plate. Annealing treatment has been performed to improve the crystallinity of the films in a quartz box with a volume of 16 cm$^3$ at various temperatures for 60 min. of kesterite CZTS.

Figure 1 shows the XRD patterns of the CZTS films annealed for 60 min. For the sample annealed at 450°C, the peaks that can be assigned to the kesterite structure were observed, showing that the CZTS crystals were successfully synthesized by this approach.

The intensity of the peaks increased when the annealing temperature up from 400 to 450°C, indicating the improvement of film crystallinity. It was found that the peaks different from those assigned to the kesterite structure started to appear at the annealing temperature of 425°C. The phases assigned from these peaks, which are different from those assigned to the kesterite structure, were considered as possible ZnSe phases at 425°C and SnS with Cu$_2$Se phases at 450°C. The increase of the CZTS peak intensity confirmed the improvement of crystallinity, which is similar to the XRD results. The low-energy shift in the CZTS peak and the decrease of the CZTS peak intensity were observed with increasing annealing temperature from 450 to 500°C, indicating the substitution of S by Se during the annealing process. It is suggested that the CZTS structure entirely decomposed to ZnS, SnS, and Cu$_{1-x}$S at 500°C. Our results indicate that the CZTS structure was unstable at high temperature, and also easily decomposed even under atmospheric pressure.

Figure 2. SEM image of the surface of the CZTS absorber before and after KCN etching.
fore (a) and after (b) KCN etching

This solar cell device configuration has been developed and used for CdZnS-based solar cells and modules and has not been specifically optimized for the CZTS absorber layers. Figure 3 depicts the J–V characteristics of the best device measured at standard test conditions. This device showed a total area efficiency of 8.0% with an open-circuit voltage of 640 mV, a short-circuit current density of 28.0 mA/cm², and fill factor of 65.8%.

Figure 3. J–V characteristics of solar cell with CZTS absorber, before (a) and after (b) KCN etching

KCN etching

To gain further insights in the device performance and loss mechanisms the external quantum efficiency (EQE) was measured on the same solar cell as shown in Figure 4. The EQE shows a steep increase around 350 nm related to the absorption edge of the ZnS window layer, a maximum value of about 70% at wavelengths between 400 and 500 nm and a subsequent broad decline for wavelengths above 520 nm (Fig.4). The optical gap of the CZTS absorber layer can be estimated from this EQE measurement, if the absorption coefficient for the material is modeled assuming a direct band gap semiconductor with parabolic bands close to the band edge. For wavelengths larger than the estimated optical gap (820 nm) significant photocurrent collection is observed in the EQE. This is likely due to substantial band tailing due to large amount of lattice disorder in the CZTS film. The collection length can be estimated by analyzing the electrical characteristics of the Al/CZTS/ZnCdS/ZnS structure. Using material parameters consistent with those commonly used for device simulation of Cu(In, Ga)Se₂ or CuInS₂ solar cells [8], the J–V and EQE characteristics can be qualitatively reproduced by assuming a bulk diffusion length below 150 nm corresponding to a density of recombination centers in the range of 10¹⁸ cm⁻³, and a space charge width of around 180 nm, corresponding to a net acceptor level of about 2.10¹⁶ cm⁻³.

Figure 4. External quantum efficiency (EQE) of solar cell with CZTS absorber, before (a) and after (b) KCN etching.

4. CONCLUSIONS

It has been shown that near-stoichiometric single-phased polycrystalline CZTS thin films can be prepared by a fast deposition process. Copper-rich growth conditions lead to the segregation of a CuS secondary phase which can be removed by KCN etching. Solar cell devices made from these CZTS layers show the currently highest device performance of CZTS based thin film solar cells fabricated by a fast deposition process with a maxi-