Cu₂ZnSnS₄ Solar Cells Fabricated by an Electrochemical Technique

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Abstract

Cu₂ZnSnS₄ (CZTS) thin films were prepared by electrochemical depositions of Cu, Sn, and Zn metal precursor layers followed by sulfurization. We found that preheating treatment for relatively long time just before the sulfurization had significant effects on qualities of final CZTS films. A solar cell based on the thus-obtained CZTS film exhibits 8% conversion efficiency.

1. Introduction

CZTS thin film solar cells have attracted considerable attention due to the use of earth-abundant and environment-friendly elements. For fabrication of the CZTS absorber, several non-vacuum processes, such as nanoparticle ink printing, sol-gel method, hydrazine-based method and electrodeposition have been widely studied [1-4]. Among them, electrodeposition is a promising process due to its technical advantages for fabrication of low-cost solar cells. For instance, electrodeposition of metallic precursor layers can usually be performed at room temperature without a heating or cooling environment using nontoxic and low-cost metal salt solutions. These solutions can also be used for a long period and recycled, thus avoiding waste of resources. Several groups have reported CZTS-based solar cells fabricated by electrodeposition. Herein, a champion solar cell based on the electrochemical route with conversion efficiency of 8% is described.

2. Experimental

Metallic precursors of Cu, Sn and Zn layers were sequentially electrodeposited on a Mo-coated soda lime glass substrate (Mo/glass). The Cu layer was deposited at -0.4 V (vs. Ag/AgCl) using an electrolating bath containing CuSO₄ 5H₂O (0.05 mol L⁻¹), citric acid (0.02 mol L⁻¹) and trisodium citrate (0.04 mol L⁻¹). The Sn layer was deposited at -0.54 V (vs. Ag/AgCl) using a bath containing Sn(II) methanesulfonate (0.05 mol L⁻¹), methanesulfonic acid (1 mol L⁻¹) and Empigen® BB detergent (n-Dodecyl-N, N-dimethylglycine, 1 mol L⁻¹). The Zn layer was deposited at -1.2 V (vs. Ag/AgCl) using a bath solution containing ZnSO₄ 7H₂O (0.1 mol L⁻¹) and K₂SO₄ (0.5 mol L⁻¹) with pH adjusted to 3 using a buffer.

The electrodeposited Cu/Zn/Sn precursor was preheated at 310 °C for various durations (0 min (i.e., without preheating), 40 min, 80 min, and 150 min) in an evacuated Pyrex ampoule. These preheated metallic precursors were sealed again in an evacuated Pyrex ampoule containing sulfur powder (5-10 mg). The ampoule was then put in a 590-°C heated furnace; after keeping it for 10 min, the ampule was ejected from the furnace for cooling.

Solar cells with a standard substrate configuration were fabricated by using CZTS films with different preheating times. On CZTS films after KCN etching, a CdS buffer layer was deposited by chemical bath deposition (CBD). Then an i-ZnO and ITO bilayer was sputtered. Finally, an Al collection grid was evaporated via a mask protection. Current density-voltage (J-V) characteristics of the solar cells were measured in air with a Bunkoh-Keiki CEP-015 photo-voltaic measurement system under a simulated amplitude modulation of AM 1.5G irradiation (100 mW cm⁻²).

3. Results and discussion

Our previous studies on fabrication of a CuInS₂ chalcopyrite film by using electrodeposition suggested that homogeneous deposition of the metallic stack is important to obtain a CuInS₂ absorber of good quality[5]. Hence, we adjusted various parameters for electrodeposition of each metallic layer, specifically for Sn and Zn depositions because the former prefers to form a lump morphology and the latter tends to become an island shape due probably to the side reaction of H₂ evolution. The resulting metallic stack showed ca. 1 μm-thick homogeneous layer (Fig. 1).

![Fig. 1 A cross-sectional SEM image of Cu-Sn-Zn stack.](image-url)

Upon preheating the metallic stack, the initial mixture of Cu, Sn, and Zn became those alloys. Regarding the morphological change analyzed by the cross-section using SEM, however, there is no appreciable difference between the films with and without preheating. When these metallic precursors were sulfurized, almost pure CZTS films were...
obtained regardless of preheating duration. On the other hand, surface SEM images of CZTS films derived from metallic precursors preheated for various durations indicated that there are significant differences in compactness and flatness between these films (Fig. 2). The surface of the CZTS film obtained from metallic precursor without preheating showed a rather rough morphology having appreciable voids. Voids and uneven surface morphology were reduced when the CZTS film was fabricated after preheating of the metallic precursor for 40 min. Surfaces of CZTS films obtained with preheating for more than 80 min tend to be flat and homogeneous. In these CZTS films, lump-structured aggregates of CZTS crystals are not obvious; instead, these crystals form compact and polish films.

By using thus-obtained CZTS films, solar cell performances were evaluated after making a device structure of Al/ITO/ZnO/CdS/CZTS/Mo/glass (without an MgF2 anti-reflection layer). As a result, all of the device parameters clearly increased with increase in preheating duration; one of the devices obtained from CZTS films derived from the metallic precursor annealed for 150 min gave the best conversion efficiency of the present solar cells (8%) with \( V_{OC} \), \( J_{SC} \) and FF values of 0.719 V, 17.7 mA cm\(^{-2} \) and 0.629, respectively (Fig. 1). To our knowledge, this is the highest reported efficiency of electrodeposited CZTS-based solar cells.

As has been reported in the literature, predominant carrier recombination would occur at the buffer-absorber (CdS-CZTS) interface in the present cell [6]. The rough surface morphology of the CZTS film results in enlargement of interface areas between the CdS buffer layer and the CZTS absorber; thus, this should limit both \( V_{OC} \) and FF of the cell derived from the CZTS film without preheating and those of the cell derived from the CZTS film with preheating for a short time. Moreover, appreciable voids of CZTS films derived from the CZTS film without preheating (Figure 2a) should act shunt paths, leading to low FF of the cell. Hence, one of the main factors for achieving high efficiency in the present device is likely to be the successful formation of a smooth CdS-CZTS interface without any significant voids passing through the CZTS film.

![Fig. 2 SEM images of CZTS films obtained by sulfurization of the metallic precursor preheated for 0-150 min.](image)

3. Conclusions

CZTS thin film solar cells with maximum conversion efficiency of 8% were successfully fabricated by electrochemical deposition of a metallic precursor followed by sulfurization. We showed the importance of preheating of the electrodeposited metallic stack composed of Cu, Sn, and Zn layers for a relatively long time just before the high-temperature sulfurization to obtain a CZTS film with good homogeneity and flatness. However, the present device still has structural failure(s). Thus, this work also suggests the possibility for further improvements in solar cell properties of the CZTS-based solar cell fabricated by a low cost and manufacturable electrodeposition.

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