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Effect of complexing agents on the electrodeposition of Cu–Zn–Sn metal precursors and corresponding Cu_2ZnSnS_4-based solar cells

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ABSTRACT

Copper zinc tin sulfide (Cu_2ZnSnS_4; CZTS) precursors were electrochemically deposited on Mo-coated glass substrates from aqueous solutions following by annealing. The effect of three complexing agents, trisodium citrate, ethylenediamine tetraacetic acid and tartaric acid, on the structural, morphological and compositional properties of CZTS thin films was investigated. The annealed thin films were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy, and energy-dispersive X-ray spectroscopy (EDS), UV–vis absorption and Raman scattering spectroscopies. XRD patterns of the synthesized films revealed the preferred orientation of the (112), (220), (200) and (312) planes, confirming the kesterite structure of CZTS. The film prepared without a complexing agent was uneven with some pores and cracks, whereas those prepared using complexing agents exhibited good coverage with some overgrown particles on the surface of the films. EDS analysis revealed that the films deposited using trisodium citrate were nearly stoichiometric for CZTS. Voltammetric studies suggested that trisodium citrate is a suitable complexing agent because it helps to align the deposition potentials of Cu, Zn, and Sn. UV–vis absorption spectra confirmed the films possessed a direct bandgap between 1.33 and 1.47 eV, which is quite close to the optimum value for a semiconductor material as an absorber in solar cells. We fabricated solar cells with the structure soda-lime glass/Mo/CZTS/CdS/i-ZnO/ZnO:Al/Al with a maximum conversion efficiency of ~2.9%.

1. Introduction

Cu_2ZnSnS_4 (CZTS) is a p-type quaternary semiconductor with a kesterite crystal structure and a promising candidate as an absorber layer in solar photovoltaic (PV) applications [1–3]. Compared with ternary compound copper indium selenide, in CZTS selenium is substituted with sulfur and the rare metal indium is replaced with zinc and tin [4,5]. Each component of CZTS is abundant in the earth's crust and possesses relatively low toxicity. CZTS possesses a high absorption coefficient in the order of $10^4\ cm^{-1}$ and direct band gap of about 1.5 eV, making it an attractive material for low-cost thin-film solar cells [6,7]. A variety of methods based on vacuum and nonvacuum techniques have been used to prepare CZTS thin films. In particular, non vacuum chemical deposition methods may allow large-scale, low-cost industrial production of such films [2,8]. Among these methods, electrochemical deposition is attractive because of its simplicity, low-cost source materials, large deposition area, inexpensive equipment and room-temperature growth compared with vacuum methods, such as evaporation and sputtering.

Electrochemical film deposition is sensitive to deposition conditions such as the deposition current density, electrode potential, and the temperature, concentration, and pH of the electrolyte solution. Codeposition of ternary alloys is quite difficult because the conditions favorable for deposition of one metal may differ from those necessary for the other constituent metals. Different metals have different deposition potentials that depend on the concentration of the constituent ions of the metal in the bath and their standard reduction potential and the presence of a complexing agent. It is well known that to successfully electrodeposit an alloy, the deposition potentials of the alloy constituents should be close to each other. Adjusting the concentration and/or adding suitable complexing agents, can, in general, be used to align deposition potentials. Complexation works by converting the simple ions of the more noble metal into complex ions with lower potential. A complexing agent may coordinate with only one of the metals to

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shift its electrode potential to the negative side while the second metal stays as a simple ion. When a complexing agent forms complexes with two types of metal ions, the potentials of both are shifted to more negative values, but the difference between them decreases. Sometimes, two different complexing agents are added to coordinate with two different metals. Complexing agents should be nontoxic and noncorrosive. To maximize stability, complexing agents are commonly added to the electrolyte solution in larger amounts than required to achieve stoichiometric composition, leaving some free complexing agent in the electrolyte.

Electrodeposition of CZTS precursors from aqueous solution in a single step is difficult because of the wide range of reduction potentials of its constituent metal ions. Ghazali et al. used a complexing agent to move the deposition potentials of metal species closer together and narrow the potential gap between the electrolyte elements to obtain a better codeposition environment and produce stoichiometric thin films of good quality. They realized that the free complexing agent in the solution during the electrodeposition process improved the lifetime of the deposition bath as well as the quality of the deposited films, including uniformity, crystallinity and adhesion of the deposited film to the substrate. Addition of ethylenediamine tetraacetic acid (EDTA) prevented the precipitation of hydroxide. The growth of SnS films using EDTA as a complexing agent has been reported [9]. Pawer et al. [10] used trisodium citrate as a complexing agent to fabricate CZTS thin films by electrodeposition in an electrolytic bath.

In this work, the effect of different additives with complexing properties on the electrodeposition of CZTS is investigated. Our research results reveal that the complexing agents in the solution have a significant effect on the Cu_2ZnSnS_4 thin films properties. The influence of these complexing agents on the structural, morphological and compositional characteristics of the prepared thin films are evaluated and discussed.

2. Experimental details

A Mo/glass substrate with a sheet resistance of ca. 20 Ω/square was used as a cathode for the electrochemical deposition of Cu, Zn, and Sn. Before deposition, the Mo/glass substrate was cleaned by sonication in acetone, followed by immersion in 25 vol% ammonia solution for 5 min to remove the molybdenum oxide layer (MoO_x) on the surface. Electrochemical deposition was performed using a conventional three-electrode system with a Mo-coated soda-lime glass substrate, Pt mesh, and saturated Ag/AgCl as working, counter and reference electrodes, respectively. The working electrode area was 0.7 cm^2. The distance between the working and counter electrodes was kept constant at about 2 cm. The CV measurements were carried out from 0 to −1.2 V (vs. Ag/AgCl) without stirring, with a scan rate 10 mV/s at room temperature for 45 min.

CZTS precursors were prepared from solutions containing 0.02 M copper (II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), 0.01 M zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$), 0.02 M tin sulfate ($SnSO_4$) and three complexing agents: tartaric acid (Aldrich, 99%, $C_4H_6O_6$, 50 mM), trisodium citrate (Aldrich, 99%, $C_6H_5Na_3O_7$, 50 mM) and EDTA (Sigma, 99%, $C_{10}H_{16}N_2O_8$, 50 mM). The pH of all solutions was adjusted to 4.75 using HCl and lactic acid. All experiments were performed at room temperature (18–20 °C). The deposited films were annealed using a three-zone tube furnace with a heating rate of 10 °C/min. Sulfur (0.5 g) was evaporated from pellets at 250 °C from a source placed in the first zone of the furnace. The sulfur vapor was transported along the furnace in a stream of N_2 + 5% H_2 gas. The samples were heated at 580 °C for 2 h in the second heating zone.

The solar cell fabrication was completed by depositing a 70 nm CdS layer grown by chemical bath deposition (CBD). The solution for CBD was prepared by mixing 400 ml of 0.42 mol CH_4N_2S aqueous solution, 60 ml of 0.05 mol CdI_2 aqueous solution and 110 ml of ammonium hydroxide solution. CBD was carried out by soaking the SLG/Mo/CZTS in the mixture for 25 min at 70–75 °C. Then it was dried at 200 °C. Followed by layers of i-ZnO (50 nm)/Al-doped n-ZnO (500 nm) films were subsequently deposited by a radio frequency magnetron sputtering method. An Al (500 nm) grid was prepared by thermal evaporation.

The structure of the films was studied by X-ray diffraction (XRD) and Raman spectroscopy. XRD patterns were obtained in the 2θ range from 20° to 80° on an X-ray diffractometer (XRD; PANalytical X'pert PRO MRD PW3040, the Netherlands) with Cu Kα radiation ($\lambda = 1.5406$ Å) using a step size of 0.02° and step time of 0.3 s. A Raman spectrometer (HR 800 UV, Jobin Yvon, France) was used to obtain Raman spectral measurements. Chemical composition and film morphology were determined by energy-dispersive X-ray spectroscopy (EDS) analysis, which was performed using a field-emission scanning electron microscope (FESEM; Nova Nano SEM 450, FEI, Japan) equipped with an EDS analyzer. The optical properties of the films were determined using an ultraviolet–visible–near infrared spectrophotometer (UV–Vis–NIR; Cary 5000-UV BROP, Agilent Technologies, Australia). Current–voltage measurements were performed in the dark and under AM1.5 (100 mW cm^2) illumination using a power meter (Keithley 2400). Device efficiency was determined using a solar simulator (SS 1000, Optical Radiation Corporation, France).

3. Results and discussion

Solution chemistry analysis was carried out to understand the complicated reactions between the metal ions and complexing agents trisodium citrate, EDTA and tartaric acid. The complexing agents were used to bring the deposition potentials of the three metals closer together and facilitate the solubilization of the various species. Cyclic voltammograms (CVs) were obtained with a scan rate of 10 mV s^{-1}. Measurements were recorded after the open-circuit voltage (V_{OC}) of the electrochemical cell had stabilized (usually after 1 h).

Fig. 1a–d shows the voltammetric responses of aqueous solutions containing Cu, Zn and Sn ions at pH 4.75 without complexing agent, and with EDTA-Na_2, tartaric acid and trisodium citrate, respectively. The electrochemical results are also summarized in Table 1. The CV of the solution lacking complexing agent exhibits Zn-reduction ($Zn^{2+} + 2e \rightarrow Zn$) and Zn-oxidation ($Zn \rightarrow Zn^{2+} + 2e$) peaks at −1.5 and −0.3 V (vs. Ag/AgCl), respectively. The CV curve also shows peaks consistent with the reduction of Sn ($Sn^{2+} + 2e \rightarrow Sn$) and oxidation of Sn ($Sn \rightarrow Sn^{2+} + 2e$) at −1.1 and −0.5 V (vs. Ag/AgCl), respectively. The reduction of Cu ($Cu^{2+} + 2e^- \rightarrow Cu$) and oxidation of Cu ($Cu \rightarrow Cu^{2+} + 2e$) are found at −1.0 and −0.8 V (vs. Ag/AgCl), respectively.

The difference between the reduction peaks of Zn and Cu is about 0.5 V without complexing agent. The reduction peaks of Zn, Sn, and Cu are found at −1.35, −1.2, and −1.0 V (vs. Ag/AgCl), respectively, when EDTA is included as a complexing agent. Adding this complexing agent slightly shifts the reduction potential of Zn to less negative potential. The reduction peak in the presence of EDTA is narrower and more intense than that obtained without additive. The difference between the reduction peaks of Zn and Cu was decreased to 0.35 V in the presence of EDTA. When tartaric acid was used as a complexing agent (Fig. 1c), the difference between the reduction peaks of Zn and Cu was 0.45 V. In contrast, this difference was just 0.25 V when trisodium citrate was used as the complexing agent (Fig. 1d). This behavior indicates that citrate has a stronger complexing effect than tartrate. The ability of trisodium citrate to bring the deposition potentials of Cu and Zn close to