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Homogeneous electrochemical deposition of in on a Cu-covered Mo substrate for fabrication of efficient solar cells with a $CuInS_2$ photoabsorber

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ABSTRACT

Electrochemical deposition of indium (In) on a copper-covered molybdenum-coated glass substrate from several acidic $InCl_3$ solutions was studied for fabrication of $CuInS_2$-based solar cells. When In was deposited using a simple acidic $InCl_3$ solution at −0.80 V (*vs.* Ag/AgCl), island-shaped growth was observed, whereas a homogeneous In film was obtained from $InCl_3$ solution containing citric acid and sodium citrate at −0.98 V (*vs.* Ag/AgCl). Electrochemical and structural analyses revealed that the citric acid additive had a function for smoothing the surface of the In deposit. The mixing with sodium citrate induced appreciable inhibition of H_2 evolution during the In deposition, leading to high current efficiency of >90%. The $CuInS_2$ film derived from the homogeneous In had a uniform thickness with a smooth surface, while the $CuInS_2$ film obtained from the island-shaped In deposit showed a large variation in thickness with recessed areas. The $CuInS_2$ film derived from the homogeneous In was showed better photoelectrochemical response than that of the film fabricated from the island-shaped In. As expected from these differences, the solar cell with an Al:ZnO/CdS/$CuInS_2$/Mo structure derived from the homogeneous In film showed the best conversion efficiency of 7.8% with relatively high reproducibility.

1. Introduction

Copper indium disulfide ($CuInS_2$) is a ternary semiconductor compound that has been studied as an absorber for thin film solar cells, due to its optimal band gap value for sunlight radiation (1.5 eV) [1], sufficiently large absorption coefficient of 3×10^5 cm^{-1} below 1000 nm [2], and efficient carrier mobility (2–20 cm^2 v^{-1} s^{-1}) [3,4]. The ideal substrate solar cell consisting of stacked layers of the $CuInS_2$ film, a thin buffer, and transparent conductive oxide (TCO) on a Mo-coated glass (Mo/glass) substrate showed highest efficiency of 11.4% [5,6]. The $CuInS_2$ absorber in a solar cell is typically prepared by sequential deposition of Cu and In metallic layers (*i.e.*, a Cu/In bilayer) on the Mo/glass substrate by vacuum methods such as sputtering and evaporation [7–9], followed by sulfurization [5–11]. However, the use of these vacuum methods leads to high equipment cost and significant losses of raw materials [12]. In order to lower electricity-generating costs of solar cells to a level competitive with commercial electricity generation, replacements of these vacuum methods with facile non-vacuum methods are promising. Hence, several non-vacuum methods, such as spraying [13–16] and electrochemical deposition [17–27], have been reported in the literature.

Among the above-mentioned non-vacuum methods, electrochemical deposition of the $CuInS_2$ film has been shown to be desirable because of its advantages, including low equipment cost, negligible waste of chemicals with utilization efficiencies close to 100%, possible formation of a compact film required for solar cell application, scalability, and manufacturability of a large-area polycrystalline film. For $CuInS_2$ film deposition, a sequential route consisting of electrochemical deposition of a Cu/In bilayer followed by sulfurization has been applied as the most usual process [19–27]. In this process, the latter sulfurization step is performed by using H_2S gas or sulfur vapor in much the same way as the above-mentioned sputtering technique. Very recently, a solar cell based on electrochemically fabricated $CuInS_2$ films has achieved conversion efficiency close to that of a cell fabricated by the vacuum process (11%) [27], indicating that the electrochemical deposition method has sufficient potential for future practical applications. For the further improvement of the conversion efficiency of the solar cell based on the electrochemically prepared $CuInS_2$ film, there is room for optimizing structures of metal staked precursors.

One of the critical problems of electrochemical deposition of a Cu/In film is the difficulty in obtaining a homogeneous In layer, *i.e.*, the In layer tends to form an island-shaped morphology using typical electrochemical deposition solutions based on both chloride and sulfate solutions [28,29]. The In island formation would be detrimental because of inductions of thickness and composition variations of resulting $CuInS_2$ films. Kinetic and mechanistic studies have shown that uncontrollable nucleation and growth of

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In metal in such simple deposition solutions induced the formation of In islands [28,29]. These facts have motivated us to find an electrochemical deposition condition to form a flat and homogeneous In layer on the Cu-deposited Mo/glass substrate. In order to achieve this objective, we focused on evaluation of the effects of organic additives on surface morphology of the thus-obtained In layer. In this study, we employed citric acid and sodium citrate as ideal organic additives to fabricate Cu/In bilayers in homogeneous In distributions. Effects of the different Cu/In film morphologies on structural, photoelectrochemical, and photovoltaic properties of the $CuInS_2$ films obtained from these Cu/In bilayers were also studied.

2. Experimental

A Mo/glass substrate with sheet resistance of *ca.* 20 Ω/square was used as a cathode for the electrochemical deposition of Cu/In bilayers. Before the deposition, the Mo/glass substrate was precleaned 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 [30]. Cu/In bilayers were deposited successively on the Mo/glass substrate by using a common three-electrode cell with a Pt foil as a counter electrode and an Ag/AgCl reference electrode under potentiostatic control using a Hokuto Denko HSV-100 potentiostat–galvanostat. Temperature of all the deposition solutions was kept at 24 ± 1 °C by immersion in a thermostated water bath. Deposition of the Cu layer was performed at −0.4 V (*vs.* Ag/AgCl) in an aqueous solution containing 10 mmol dm^{-3} $CuSO_4$ and 10 mmol dm^{-3} citric acid (pH 2.3) [26]. The amount of deposited Cu metal was controlled by the total electric charge at 0.83 C cm^{-2} using a Hokuto Denko HF-201A coulomb/ampere hour meter. For deposition of the In layer onto the top of the Cu-deposited Mo/glass (Cu/Mo/glass), three kinds of acidic solutions with pH adjusted to 2.2 by a concentrated HCl solution were used in this study: one was a 12 mmol dm^{-3} $InCl_3$ solution (In-bath(A)) [26], another was a 30 mmol dm^{-3} $InCl_3$ solution containing 10 mmol dm^{-3} citric acid (In-bath(B)), and the other consisted of 30 mmol dm^{-3} $InCl_3$, 10 mmol dm^{-3} citric acid, and 35 mmol dm^{-3} sodium citrate (In-bath(C)) [31]. Applied potentials for the In deposition were adjusted to −0.80 V (*vs.* Ag/AgCl) for In-bath(A) and −0.98 V (*vs.* Ag/AgCl) for In-bath(B) and In-bath(C). The total charge during the In deposition was fixed at 0.96 C cm^{-2}, irrespective of the kind of In solution used. Amounts of deposited In metals thus-formed were quantified by measuring the changes in weights of the Cu/Mo/glass substrates before and after In deposition. As separate experiments, contributions of H_2 evolution during the In deposition were studied using aqueous HCl solutions (pH 2.2) containing 10 mmol dm^{-3} citric acid and containing 10 mmol dm^{-3} citric acid and 35 mmol dm^{-3} sodium citrate (see below).

Sulfurization of as-prepared Cu/In bilayer films to form $CuInS_2$ films was performed by using a three-step temperature profile as reported previously [26], with slight modifications. First, the Cu/In bilayer films were heated to 110 °C in Ar, and then heating at this temperature was continued for 60 min. In the second step, the film treated at 110 °C was heated to 520 °C in Ar using a heating ramp of 25 °C min^{-1}. Finally, sulfurization of the film was performed by introduction of H_2S (5% in Ar) at 520 °C for 10 min, and then the film was allowed to cool down to ambient temperature in Ar or H_2S (5% in Ar). Since all of the Cu/In bilayer films had relatively Cu-rich compositions, the $CuInS_2$ films thus-formed include a Cu_xS impurity component: these films were treated with a 10% KCN solution to remove the Cu_xS component [5].

Surface and cross-sectional morphologies of the Cu, Cu/In, and $CuInS_2$ films prepared were examined using a Hitachi S-5000 FEG scanning electron microscope (SEM). X-ray diffraction (XRD) patterns were measured using a Rigaku MiniFlex X-ray diffractometer (Cu Kα, Ni filter).

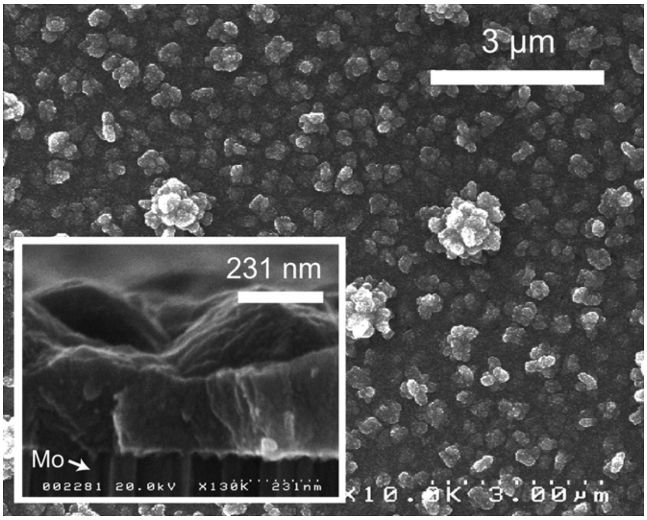

Fig. 1. A top view SEM image of an electrochemically deposited Cu film. Inset shows the corresponding cross-sectional image.

Photoelectrochemical properties of $CuInS_2$ films were measured in an aqueous solution containing 0.1 mmol dm^{-3} $Eu(NO_3)_3$ as an electron acceptor at pH 4. A Pyrex electrolytic cell having a flat window was used. The photocurrent response of the film was measured under potentiostatic control using a three-electrode system with a Pt foil counter electrode and an Ag/AgCl reference electrode. Transient photocurrents at potentials ranging from 0.2 V to −0.45 V (*vs.* Ag/AgCl) were measured using the lock-in technique under chopped illumination of 600 nm monochromatic light. Photocurrent external quantum efficiency (EQE) spectra at the potential of −0.4 V (*vs.* Ag/AgCl) were also measured using the lock-in technique under chopped illumination of monochromatic light (400–900 nm). The number of incident photons was determined by an OPHIR Orion Laser power meter equipped with a photodiode. All the photoelectrochemical measurements were performed under N_2 purging.

For evaluation of solar cell properties of the $CuInS_2$ films, the films were processed to form an Al:ZnO/CdS/CIS/Mo/glass structure. On the $CuInS_2$ films, a CdS buffer layer was deposited by chemical bath deposition (CBD) [26], and an Al:ZnO window layer was then deposited on the top of the CdS layer by radio frequency (RF) magnetron sputtering [26,32]. Current density–voltage (*J*–*V*) characteristics under simulated AM1.5 irradiation (100 mW cm^{-2}) through the Al:ZnO window layer and those under dark of thus-obtained solar cells were measured with a Bunkoh–Keiki CEP–015 photovoltaic measurement system.

3. Results and discussion

3.1. Effects of additives for In deposition

Fig. 1 shows a typical SEM image of the Cu film on Mo/glass. The top view image shows that the surface of the film has a rugged morphology composed of small lumps of several hundred nanometers in size. The corresponding cross-sectional image of the Cu film shown in inset of Fig. 1 shows the formation of a condensed film at the bottom layer with a thickness of *ca.* 250 nm, while the upper part has a bumpy structure, as expected from the surface morphology. Since there is no appreciable crack or pinhole in the Cu film, we employed this film as the substrate (*i.e.*, the Cu/Mo/glass substrate) for successive electrochemical deposition of In. Results