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# Homogeneous electrochemical deposition of in on a Cu-covered Mo substrate for fabrication of efficient solar cells with a CuInS<sub>2</sub> photoabsorber

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# ABSTRACT

Electrochemical deposition of indium (In) on a copper-covered molybdenum-coated glass substrate from several acidic InCl<sub>3</sub> solutions was studied for fabrication of CuInS<sub>2</sub>-based solar cells. When In was deposited using a simple acidic InCl<sub>3</sub> solution at -0.80 V (*vs.* Ag/AgCl), island-shaped growth was observed, whereas a homogeneous In film was obtained from InCl<sub>3</sub> 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<sub>2</sub> evolution during the In deposition, leading to high current efficiency of >90%. The CuInS<sub>2</sub> film derived from the homogeneous In had a uniform thickness with a smooth surface, while the CuInS<sub>2</sub> film obtained from the island-shaped In deposit showed a large variation in thickness with recessed areas. The CuInS<sub>2</sub> 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<sub>2</sub>/Mo structure derived from the homogeneous In film showed the best conversion efficiency of 7.8% with relatively high reproducibility.

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## 1. Introduction

Copper indium disulfide (CuInS<sub>2</sub>) 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  $3 \times 10^5 \text{ cm}^{-1}$ below 1000 nm [2], and efficient carrier mobility (2-20 cm<sup>2</sup> v<sup>-1</sup> s<sup>-1</sup>) [3,4]. The ideal substrate solar cell consisting of stacked layers of the CuInS<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>S gas or sulfur vapor in much the same way as the abovementioned sputtering technique. Very recently, a solar cell based on electrochemically fabricated CuInS<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> films obtained from these Cu/In bilayers were also studied.

## 2. Experimental

A Mo/glass substrate with sheet resistance of *ca*. 20  $\Omega$ /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 threeelectrode 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  $24 \pm 1$  °C by immersion in a thermostated water bath. Deposition of the Cu layer was performed at -0.4V (vs. Ag/AgCl) in an aqueous solution containing  $10 \text{ mmol dm}^{-3} \text{ CuSO}_4$  and  $10 \text{ mmol dm}^{-3}$  citric acid (pH 2.3) [26]. The amount of deposited Cu metal was controlled by the total electric charge at 0.83 C cm<sup>-2</sup> 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  $12 \text{ mmol dm}^{-3} \text{ InCl}_3$ solution (In-bath(A)) [26], another was a 30 mmol  $dm^{-3}$  InCl<sub>3</sub> solution containing 10 mmol dm<sup>-3</sup> citric acid (In-bath(B)), and the other consisted of 30 mmol dm<sup>-3</sup> InCl<sub>3</sub>, 10 mmol dm<sup>-3</sup> citric acid, and 35 mmol dm<sup>-3</sup> sodium citrate (In-bath(C)) [31]. Applied potentials for the In deposition were adjusted to -0.80 V (vs. Ag/AgCl) for Inbath(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<sup>-2</sup>, 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<sub>2</sub> evolution during the In deposition were studied using aqueous HCl solutions (pH 2.2) containing 10 mmol dm<sup>-3</sup> citric acid and containing 10 mmol dm<sup>-3</sup> citric acid and 35 mmol dm<sup>-3</sup> sodium citrate (see below).

Sulfurization of as-prepared Cu/In bilayer films to form CuInS<sub>2</sub> 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<sup>-1</sup>. Finally, sulfurization of the film was performed by introduction of H<sub>2</sub>S (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<sub>2</sub>S (5% in Ar). Since all of the Cu/In bilayer films had relatively Cu-rich compositions, the CuINS<sub>2</sub> films thus-formed include a Cu<sub>x</sub>S impurity component: these films were treated with a 10% KCN solution to remove the Cu<sub>x</sub>S component [5].

Surface and cross-sectional morphologies of the Cu, Cu/In, and CuInS<sub>2</sub> films prepared were examined using a Hitachi S-5000 FEG scanning electron microscope (SEM). X-ray diffraction (XRD)



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

patterns were measured using a Rigaku MiniFlex X-ray diffractometer (Cu K $\alpha$ , Ni filter).

Photoelectrochemical properties of CuInS<sub>2</sub> films were measured in an aqueous solution containing 0.1 mmol dm<sup>-3</sup> Eu(NO<sub>3</sub>)<sub>3</sub> 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<sub>2</sub> purging.

For evaluation of solar cell properties of the CuInS<sub>2</sub> films, the films were processed to form an Al:ZnO/CdS/CIS/Mo/glass structure. On the CuInS<sub>2</sub> 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<sup>-2</sup>) 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



**Fig. 2.** Linear sweep voltammograms in (a) In-bath(A), (b) In-bath(B), and (c) In-bath(C) obtained by using the Cu deposited Mo/glass substrate.

of further studies on morphological controls of the Cu film were reported previously [33].

Fig. 2 shows linear sweep voltammetry (LSV) plots obtained with the Cu deposited Mo/glass substrate immersed in In-bath(A), In-bath(B), and In-bath(C) solutions. The potential sweep started at -0.1 V vs. Ag/AgCl and was performed in the cathodic direction with a scan rate of 10 mV s<sup>-1</sup>. In all LSV plots, remarkable rises in cathodic currents at potentials more negative than -0.65 V (vs. Ag/AgCl) were observed. Since the redox potential of the  $In^{3+}/In$  couple is -0.54 V (vs. Ag/AgCl), these rises are likely to be due to the reduction of In<sup>3+</sup> ions. It is clear that almost the same current onset for the In<sup>3+</sup> reduction was observed irrespective of presences of citric acid and sodium citrate in the solution, suggesting no appreciable formation of citrate complexes in the present system. Based on the fact that appreciable cathodic currents seem to appear at applied potentials more negative than -0.70 V (vs. Ag/AgCl), we fabricated In films at applied potentials more negative than this potential (*i.e.*, -0.80 V (vs. Ag/AgCl) for In-bath(A) and -0.98 V (vs. Ag/AgCl) for Inbath(B) and In-bath(C)). It should be noted that appreciable bobbles were also evolved by applying such negative potentials, indicating significant contribution of water reduction to the observed cathodic currents (see below).

Fig. 3 shows SEM images of In films formed on the Cu/Mo/glass substrate from In-bath(A), In-bath(B), and In-bath(C) solutions. The SEM image of the In film obtained from In-bath(A) shows inhomogeneous distributions of In deposits having many crevices between their grains (Fig. 2a). As can be seen in Fig. 3d, the corresponding cross-sectional SEM image shows a very rough structure: thicknesses of the film depend strongly on the area from *ca*. 200 nm to ca. 800 nm, as expected from the surface morphology. On the other hand, when the In-bath(B) solution containing an organic additive of citric acid was used instead of In-bath(A), the morphology of the surface of the In film thus-obtained was smooth (Fig. 3b). The cross-sectional image of the film in Fig. 3e also indicates the occurrence of uniform growth to make a condensed In film with large grains of over 1  $\mu$ m in breath and 550–600 nm in thickness. A uniform In film with similar morphology was also obtained by using In-bath(C), which contains citric acid and sodium citrate, as shown in Fig. 3c and f. These results suggest that the citric acid additive has a function to smooth the surface of the In film.

Fig. 4 shows XRD patterns of Cu/In bilayers on Mo/glass obtained from In-bath(A) and In-bath(C) solutions. In addition to the intense reflection derived from the Mo film, both samples showed several diffraction peaks assignable to In, Cu, and a CuIn alloy. Significantly weak reflections derived from Cu metal on both samples suggest a less crystalline nature of the Cu layer. It is known that metallic In easily diffuses into metallic Cu and forms intermetallic compounds [25]. Thus, appreciable amounts of the CuIn alloy were formed on both samples even at ambient temperature. Based on the fact that reflections derived from the CuIn alloy appeared predominantly in the XRD patterns of In-deposited samples after a short electrochemical deposition period (less than 0.3 C cm<sup>-2</sup>, data not shown), CuIn alloy formation is preferable at the initial stage of electrochemical deposition of In.

Previous studies on electrochemical deposition of In in acidic solutions without any organic additives have suggested that growth of the In layer on Cu/Mo/glass follows a two-step behavior: formation of a continuously smooth thin film followed by three-dimensional (3D) growth to form an island-shaped surface morphology [28,29]. The former smooth film formation results from the rapid interdiffusion between Cu and In, leading to layerby-layer growth of the Culn alloy without nucleation, and the latter



Fig. 3. SEM images of electrochemically deposited In films from (a, d) In-bath(A), (b, e) In-bath(B), and (c, f) In-bath(C): (a-c) top views and (d-f) cross-sectional views.



**Fig. 4.** XRD patterns of electrochemically deposited Cu/In bilayers from (a) In-bath(A) and (b) In-bath(C).

typical 3D growth is likely to be followed by instantaneous nucleation limited by diffusion. The above-described XRD results suggest that growth of In layers in the present study followed the same mechanism, regardless of the presence of organic additives. Hence, the citric acid in acidic solution should play a role in suppression of island-shaped growth of In onto the preformed Cu/In alloy layer at the second stage during the In deposition. One probable reason for the function of citric acid is reduction of the overpotential of In deposition induced by adsorption onto the Cu/In alloy surface to reduce its surface energy. This function should enhance nucleation probability, resulting in the formation of a smooth surface. In addition, the enhancement of nucleation can be explained by the difference in the applied potential, *i.e.*, the In deposition in In-bath(B) and In-bath(C) solutions was performed at a relatively negative potential (-0.98 V (vs. Ag/AgCl)) compared to that in the In-bath(A) solution (-0.80 V (vs. Ag/AgCl)). However, the fact that a similar rough surface morphology was obtained on the Cu/In bilayer from the In-bath(A) solution even at -0.98 V (vs. Ag/AgCl) indicates an intrinsic effect of citric acid on the homogeneous In deposition. It should also be noted that the application of such a highly negative potential for the In-bath(A) solution often leads to partial peeling of the Cu/In bilayer probably due to the evolution of considerable amounts of hydrogen (H<sub>2</sub>) (see below). Hence, the use of relatively less potential of -0.80 V (vs. Ag/AgCl) is a suitable condition for In deposition from the In-bath(A) solution.

Current efficiencies of the In deposition from different solutions were calculated by measuring weights of In deposits. When the In deposition was performed using In-bath(A) solution at -0.80 V (vs. Ag/AgCl), the efficiency only reached 60%. Similar current efficiency was also obtained when the In-bath(B) solution was used with applied potential of -0.98 V (vs. Ag/AgCl), even though a smooth In film without crevices was formed. On the other hand, In

deposition from the In-bath(C) solution at -0.98 V (vs. Ag/AgCl) showed a high current efficiency of more than 90%. Since applied potentials of these In depositions are much more negative than the equilibrium potential of the H<sub>2</sub>/H<sup>+</sup> couple (-0.35 V (vs. Ag/AgCl) at pH 2.2), those current efficiencies should strongly depend on the degree of contribution of H<sub>2</sub> evolution.

In order to evaluate roles of organic additives for the current efficiency, current density measurements of H<sub>2</sub> evolution from acidic chloride solutions (pH 2.2) with or without citric acid and/or sodium citrate were performed. Since the substrate surface should change from Cu to In through the intermetallic CuIn alloy (see above), we employed Cu/Mo/glass, CuIn/Cu/Mo/glass, and In/CuIn/Cu/Mo/glass substrates for the H<sub>2</sub> evolution experiment. CuIn/Cu/Mo/glass and In/CuIn/Cu/Mo/glass substrates were obtained by deposition of In for a short period (*ca.*  $0.3 \,\mathrm{C \, cm^{-2}}$ ) and a long period (*ca.*  $0.9 \text{ C cm}^{-2}$ ) using In-bath(A), In-bath(B), and In-bath(C) solutions. Table 1 summarizes current densities on these substrates in three different solutions, *i.e.*, aqueous HCl, that containing 10 mmol dm<sup>-3</sup> citric acid, and that containing 10 mmol dm<sup>-3</sup> citric acid and 35 mmol dm<sup>-3</sup> sodium citrate. Irrespective of solution compositions, relatively high current densities were observed on the Cu/Mo/glass substrate; it is clear that addition of both citric acid and sodium citrate induces significant enhancement of H<sub>2</sub> evolution on this substrate. On the other hand, a suppressive effect of citric acid addition on H<sub>2</sub> evolution appeared when we used CuIn/Cu/Mo/glass and In/CuIn/Cu/Mo/glass substrates, *i.e.*, moderate current densities comparable to those in the simple HCl solution at -0.80 V (vs. Ag/AgCl) were observed in the citric acid solution even at relatively high applied potential (-0.98 V (vs. Ag/AgCl)). Furthermore, H<sub>2</sub> evolution currents on these substrates were significantly suppressed in the presence of both citric acid and sodium citrate: current densities in the solution at -0.98 V (vs. Ag/AgCl) were only about half of those in the simple HCl solution at -0.80 V (vs. Ag/AgCl). As discussed above, the surface of the Cu/Mo/glass substrate should be covered with the CuIn alloy layer in a short period during In deposition. Thus, the surface composition of the substrate during In deposition should be the CuIn alloy or the In metal in almost all the deposition durations. The high current efficiency of In deposition achieved in the In-bath(C) solution as mentioned above is, therefore, explained by the efficient suppression behavior.

For further evaluation of the efficient suppression of  $H_2$  evolution in the HCl solution containing both citric acid and sodium citrate, effects of inorganic sodium salts, *e.g.*, NaCl, KCl, Na<sub>2</sub>SO<sub>4</sub>, and Na<sub>2</sub>CO<sub>3</sub>, in the acidic citric acid solution, instead of sodium citrate, on the  $H_2$  evolution properties were examined by using Culn/Cu/Mo/glass substrates. As a result, addition of these salts was found to be ineffective for suppression of  $H_2$  evolution. Moreover, an increase in the concentration of citric acid had a detrimental effect. Based on the fact that all of the carboxyl protons are not fully dissociated in the present pH range, the difference between sodium citrate and citric acid could not be rationally understood. At present, the efficient suppression of  $H_2$  evolution over Culn and In

#### Table 1

Current densities for H<sub>2</sub> evolution on several substrates under various conditions.

substrates	Current density (mA cm <sup>-2</sup> )						
	None <sup>a</sup> (-0.80 V) <sup>d</sup>	None <sup>a</sup> (-0.98 V) <sup>d</sup>	$CA^{b} (-0.98 V)^{d}$	$CA^{b} + SC^{c} (-0.98 V)^{d}$			
Cu/Mo/glass	1.36	1.74	3.20	6.02			
CuIn/Cu/Mo/glass	0.45	0.64	0.40	0.24			
In/CuIn/Cu/Mo/glass	0.13	0.17	0.10	0.07			

<sup>a</sup> Aqueous HCl solution (pH 2.2) without any additives.

<sup>b</sup> Aqueous HCl solution containing 10 mmol dm<sup>-3</sup> citric acid (pH 2.2).

 $^{\rm c}\,$  Aqueous HCl solution containing 10 mmol dm  $^{-3}$  citric acid and 35 mmol dm  $^{-3}\,$  sodium citrate (pH 2.2).

<sup>d</sup> Applied potentials referred to the Ag/AgCl electrode.



Fig. 5. XRD patterns of  $CuInS_2$  films derived from electrochemically deposited Cu/In bilayers in (a) In-bath(A) and (b) In-bath(C) solutions.

surfaces in the present acidic mixture of HCl, citric acid, and sodium citrate is likely to be due to a concerted mechanism of components in the solution.

## 3.2. Structural characterizations of sulfurized CuInS<sub>2</sub> films

The Cu/In bilayers with different In morphologies, which were obtained from In-bath(A) and In-bath(C) solutions, were converted into CuInS<sub>2</sub> films (labeled CuInS<sub>2</sub>(A) and CuInS<sub>2</sub>(C), respectively) by sulfurization in H<sub>2</sub>S (5% in Ar) at 520 °C followed by chemical etching of a Cu<sub>x</sub>S component. As shown in Fig. 5, XRD analyses of thus-obtained CuInS<sub>2</sub>(A) and CuInS<sub>2</sub>(C) films indicate typical diffraction peaks of (112), (004)/(200), (204)/(220), and (116)/(312) reflections that coincide with CuInS<sub>2</sub> crystal with a chalcopyrite structure (JCPDS 27-0159) [6] and no appreciable detection of any secondary phases, except for the Mo substrate. The fact that the Cu/In/S composition ratios of these films were confirmed to be almost stoichiometric (i.e., 24/25/51) also indicates formation of films having a single CuInS<sub>2</sub> phase. On both films, moreover, the intensity of the major peak at  $2\theta = 27.8^{\circ}$ , corresponding to the (112) plane, was much stronger than those of others derived from (200) and (204)/(220) planes, indicating preferable (112) orientation. In addition, the CuInS<sub>2</sub>(C) film showed more intense reflections than those of the CuInS<sub>2</sub>(A) film (e.g., the intensity of (112) reflection of CuInS<sub>2</sub>(C) was *ca.* 1.2 times larger than that of CuInS<sub>2</sub>(A)), suggesting that the former film achieves a relatively large grain growth in comparison with that of the latter one

Fig. 6 shows SEM images of CuInS<sub>2</sub>(A) and CuInS<sub>2</sub>(C). Top view SEM images of both films indicate that they consist of angularshaped microcrystallites, as shown in Fig. 6a and b. It is clear that the CuInS<sub>2</sub>(A) film has appreciable recessed areas (Fig. 6a), while a relatively flat surface composed of compact agglomerates was observed in the SEM image of the CuInS<sub>2</sub>(C) film (Fig. 6b). The significant differences in surface roughness between these films should be due to morphological differences of Cu/In bilayers before sulfurization. As expected from these surface morphologies, the CuInS<sub>2</sub>(A) film showed a relatively large variation of thicknesses compared to that of the CuInS<sub>2</sub>(C) film. Moreover, the size of each CuInS<sub>2</sub> grain in the  $CuInS_2(C)$  film is larger than that in the  $CuInS_2(A)$  film, which is in good agreement with the above-described XRD results. Another point worth noting is that CuInS<sub>2</sub>(C) appears to have relatively poor adherence compared to that of  $CuInS_2(A)$ , though both of the films have negligible voids between CuInS<sub>2</sub> crystallites. The flat surface and well-grown crystallite without voids of the  $CuInS_2(C)$ 



**Fig. 6.** (a, b) Top view and (c, d) cross-sectional view SEM images of  $CulnS_2$  films derived from electrochemically deposited Cu/In bilayers in (a, c) In-bath(A) and (b, d) In-bath(C).



**Fig. 7.** Photocurrent-potential curves of (a) CulnS<sub>2</sub>(A) and (b) CulnS<sub>2</sub>(C) films in a 0.1 mol dm<sup>-3</sup> Eu<sup>3+</sup> aqueous solution at pH 4.

film would be beneficial for solar cell application, but the poor adherence would be detrimental because of the increment in series resistance: details of these effects are discussed below.

## 3.3. Photoelectrochemical properties

Fig. 7 shows photocurrent-potential curves of CuInS<sub>2</sub> films taken in a solution containing Eu<sup>3+</sup> as an electron acceptor. Owing to *p*-type semiconductive characters, cathodic photocurrents were observed and their magnitude increased with negative shifts of the potential. Although the onset potential of photocurrents observed on both films was essentially the same (ca. -0.05 V (vs. Ag/AgCl)), the CuInS<sub>2</sub>(C) film showed relatively large photocurrents, suggesting higher film quality than that of the CuInS<sub>2</sub>(A) film. As shown in Fig. 8, corresponding EQE spectra of photocurrent on both film measured at -0.4 V (vs. Ag/AgCl) also indicated better photoelectrochemical response of the  $CuInS_2(C)$  film than that of the  $CuInS_2(A)$ film. It is noted that both films showed almost the same onset wavelength, *i.e.*, band gap energies  $(E_g s)$  of these films determined from intercepts of the photon energy  $(h\nu)$  axis of  $(EQE \times h\nu)^2 - h\nu$  plots [34] (not shown) were equivalent (ca. 1.5 eV). The value is also in good agreement with the reported  $E_g$  value of CuInS<sub>2</sub> films [1].

The EQE value is correlated with the width of the space charge layer (W) as follows [35]:

$$EQE = 1 - \exp(-\alpha W), \tag{1}$$



**Fig. 8.** EQE spectra of cathodic photocurrents obtained on (a) CulnS<sub>2</sub>(A) and (b) CulnS<sub>2</sub>(C) films. The measurement was carried out at -0.4 V (vs. Ag/AgCl) in a 0.1 mol dm<sup>-3</sup> Eu(NO<sub>3</sub>)<sub>3</sub> aqueous solution at pH 4.



**Fig. 9.** J-V characteristics of Al:ZnO/CdS/CulnS<sub>2</sub>/Mo/glass cells. These cells were made from CulnS<sub>2</sub> films obtained from (a) ln-bath(A) and (b) ln-bath(C). CP denotes the crossing point of illuminated and dark J-V curves.

where  $\alpha$  denotes absorption coefficient. This equation indicates possible estimation of *W* from a slope of  $-\ln(1 - EQE)$  vs.  $\alpha$  plot. Using  $\alpha$  values at wavelengths close to photoabsorption onset [36] *W* values of CuInS<sub>2</sub>(A) and CuInS<sub>2</sub>(C) films at an applied potential (*E*) of -0.4 V (vs. Ag/AgCl) were estimated to be 0.10  $\mu$ m and 0.17  $\mu$ m, respectively. The accepter density (*N*<sub>a</sub>) is correlated with *W* by

$$W = \left\{ \frac{2(E_{\rm FB} - E)\varepsilon_0 \varepsilon_{\rm r}}{qN_{\rm a}} \right\} \frac{1}{2},\tag{2}$$

where,  $E_{\rm FB}$ ,  $\varepsilon_0$ ,  $\varepsilon_r$ , and q are flatband potential, dielectric constant of the vacuum, the relative dielectric constant of CuInS<sub>2</sub> film, and electric charge, respectively. Since the photocurrent onset of a ptype semiconductor is likely to occur at potentials of *ca*. 0.2–0.3 V more negative than  $E_{\rm FB}$  [35,37–39] the  $E_{\rm FB}$  of CuInS<sub>2</sub> in the present electrolyte solution would lie at *ca*. 0.15–0.25 V (*vs*. Ag/AgCl) (see Fig. 7). Moreover, assuming that  $\varepsilon_r$  of CuInS<sub>2</sub> is [10,35,40]  $N_a$ s of CuInS<sub>2</sub>(A) and CuInS<sub>2</sub>(C) films were calculated to be 6.8–7.2 × 10<sup>16</sup> and 2.1–2.5 × 10<sup>16</sup>, respectively. The  $N_a$ s of chalcopylite films for efficient solar cells were in the order of 10<sup>16</sup> cm<sup>-3</sup> [41–43]. Hence,  $N_a$  values of present CuInS<sub>2</sub> films would be preferable to apply the use of solar cell as discussed below.

## 3.4. Solar cell properties

device Solar cells with а structure of Al:ZnO/CdS/CuInS<sub>2</sub>/Mo/glass (without an antireflection coating) were prepared by depositing CdS and Al:ZnO layers on CuInS<sub>2</sub>(A) and CuInS<sub>2</sub>(C). The light and dark *I–V* characteristics and cell parameters obtained from these *I*-V curves are shown in Fig. 9 and Table 2, respectively. The solar cell derived from CuInS<sub>2</sub>(C) exhibits good performance with conversion efficiency ( $\eta$ ) of 7.8% (Fig. 9b) compared to that of the cell based on CuInS<sub>2</sub>(A) ( $\eta$  = 4.4%, Fig. 9a). It should be noted that the  $\eta$  values of the former cells were relatively constant (more than 7%), whereas those of the latter cells were significantly deviated in the range of about 4-7% despite

#### Table 2

Solar cell parameters obtained from illuminated *J-V* curves shown in Fig. 8.

Photo-absorber	$J_{\rm SC}^{\rm a}$ (mA cm <sup>-2</sup> )	$V_{\rm OC}{}^{\rm b}({\rm V})$	FF <sup>c</sup>	$\eta^{ m d}$ (%)	$R_{\rm s}^{\rm e}$ ( $\Omega  {\rm cm}^2$ )	$R_{\rm sh}{}^{\rm f}({\rm k}\Omega{\rm cm}^2)$
$\begin{array}{c} CuInS_2(A) \\ CuInS_2(C) \end{array}$	16.0	0.57	0.49	4.4	10.2	2.48
	21.3	0.67	0.55	7.8	8.0	3.69

<sup>a</sup> Short-circuit current density.

<sup>b</sup> Open circuit voltage.

<sup>c</sup> Fill factor.

 $^{\rm d}\,$  Conversion efficiency.

<sup>e</sup> Series resistance.

<sup>f</sup> Shunt resistance.

applying the same procedure. The insufficient reproducibility of the cell based on the  $CuInS_2(A)$  film is due to the poor homogeneity of  $CuInS_2$ , *e.g.*, large thickness variations and inhomogeneous composition distributions, leading to reduced cell parameters.

In accordance with the above photoelectrochemical measurements, the  $CuInS_2(C)$  film should have more efficient carrier utilization properties than that of the CuInS<sub>2</sub>(A) film (see Figs. 7 and 8). As discussed above, this would be due to better structural properties and electric properties of the  $CuInS_2(C)$  film (flat surface, well-grown crystallite, and relatively small  $N_a$ ) than those of the CuInS<sub>2</sub>(A) film. These resulted in relatively small series resistance of the cell derived from CuInS<sub>2</sub>(C), thus leading relatively large short-circuit current density  $(I_{SC})$  and fill factor (FF). Another difference in cell parameters between the CuInS<sub>2</sub>(A)-based cell and the CuInS<sub>2</sub>(C)-based cell summarized in Table 2 is open circuit voltages ( $V_{OC}$ s). As has been reported in the literature [42–44] the buffer-absorber (CdS-CuInS<sub>2</sub>) interface is considered to be a "cliff-type" band alignment, which differs from the "notch-type" alignment of the CdS–Cu(In,Ga)Se<sub>2</sub> interface. Since N<sub>a</sub>s of present CuInS<sub>2</sub> films are of the same order as those reported in studies on the band alignment calculations (e.g., the  $N_a$  value of  $5 \times 10^{16}$  was given in the literature [43]), Fermi levels of present CuInS<sub>2</sub> films should be comparable to that in the literature. Hence, the reported "cliff-type" band alignment can be applied to present materials. In such a band alignment, it is known that interface recombination is dominant in the present cell [43,44]. As discussed above, the rough surface morphology of the CuInS<sub>2</sub>(A) film results in enlargement of interface areas between the CdS buffer layer and the CuInS<sub>2</sub> absorber; thus, this should limit  $V_{OC}$  as well as FF of the cell. In addition, V<sub>OC</sub> of an illuminated solar cell depends on the ratio of the active area  $(A_a)$  and the total area  $(A_t)$  of the junction interface, *i.e.*, as the  $A_a/A_t$  ratio increases,  $V_{OC}$  tends to decrease [45,46]. Since microscopic roughness of the junction interface increases  $A_{\rm f}$  but not  $A_a$ , high  $V_{OC}$  can be obtained by a cell having a smooth junction interface. Hence, the  $CuInS_2(C)$  film having a relatively smooth CdS–CuInS<sub>2</sub> interface achieved larger V<sub>OC</sub> than that obtained for the cell based on the CuInS<sub>2</sub>(A) film.

Further inspection of the solar cell parameters shown in Table 2 indicates that a limiting factor of the present best cell derived from the CulnS<sub>2</sub>(C) film is its small FF, as a result of high series resistance ( $R_s$ ) as compared to several literature devices. As discussed above, the CulnS<sub>2</sub>(C) film showed relatively poor adhesion; high  $R_s$  is speculated to be mainly due to high interfacial resistance between the CulnS<sub>2</sub>(C) film and the Mo substrate. The observation of cross-over behavior at a lower current than that observed on the cell derived from CulnS<sub>2</sub>(A) (Fig. 9) supports this hypothesis. In order to obtain further increase in solar cell performance of the present device, therefore, optimization of sulfurization parameters to improve adhesion is required.

## 4. Conclusion

In this study, the effects of additions of certain amounts of citric acid and sodium citrate to an acidic InCl<sub>3</sub> solution on the formation

of a smooth and homogeneous In film on the surface of a Cu-covered Mo/glass substrate were examined. Homogeneous electrochemical deposition of In was found to be achieved by efficient enhancement of the In nucleation induced by citric acid, whereas the addition of sodium citrate was effective for reduction of H<sub>2</sub> evolution, a side reaction. Photoelectrochemical analyses of CuInS<sub>2</sub> films obtained by sulfurization of Cu/In bilayers revealed that relatively high quality film was obtained from the homogeneous In film compared to the film derived from the inhomogeneous In island film. As expected the solar cell with a Al:ZnO/CdS/CuInS<sub>2</sub>/Mo structure derived from the homogeneous In was shown to be more efficient than the cell derived from the inhomogeneous In. Hence, we have proved the importance of structural controls of the In precursor film to obtain an efficient CuInS2-based solar cell. Since the basic idea should be applicable to other thin-film compound solar cells based on Cu(In,Ga)Se<sub>2</sub> (CIGS) and Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) absorbers, studies are now in progress to find optimal conditions of electrochemical depositions in order to obtain smooth and homogeneous metallic precursor stacks for solar cell applications.

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#### References

- M.A. Green, K. Emery, D.L. King, S. Igari, W. Warta, Progress in Photovoltaics: Research and Applications 10 (2002) 355–360.
- [2] F.C. Akkari, R. Brini, M. Kanzari, B. Rezig, Journal of Materials Science 40 (2005) 5751–5755.
- [3] L.L. Kazmerski, M.S. Ayyagari, G.A. Sanborn, Journal of Applied Physics 46 (1976) 4865–4869.
- [4] Y.B. He, T. Krämer, I. Österreicher, A. Polity, B.K. Meyer, M. Hardt, Semiconductor Science and Technology 20 (2005) 685–692.
- [5] J. Klaer, J. Bruns, R. Henninger, K. Siemer, R. Klenk, K. Ellmer, D. Bräunig, Semiconductor Science and Technology 13 (1998) 1456–1458.
- [6] K. Siemer, J. Klaer, I. Luck, J. Bruns, R. Klenk, D. Bräunig, Solar Energy Materials and Solar Cells 67 (2001) 159–166.
- [7] S. Bandyopadhyaya, S. Chaudhuri, A.K. Pal, Solar Energy Materials and Solar Cells 60 (2000) 323–339.
- [8] C.V. Klopmann, J. Djordjevic, E. Rudigier, R. Scheer, Journal of Crystal Growth 289 (2006) 121–133.
- [9] J. Klaer, R. Klenk, H.-W. Schock, Thin Solid Films 515 (2007) 5929-5933.
- M. Krunks, O. Bijakina, T. Varema, V. Mikli, E. Mellikov, Thin Solid Films 338 (1999) 125–130.
   B. Ghard, J. Kurst, A. Kurst, N. Maura, H. Böhla, Thia
- [11] R. Klenk, J. Klaer, R. Scheer, M.C. Lux-Steiner, I. Luck, N. Meyer, U. Rühle, Thin Solid Films 480–481 (2005) 509–514.
- [12] C.J. Hibberd, E. Chassaing, W. Liu, D.B. Mitzi, D. Lincot, A.N. Tiwari, Progress in Photovoltaics: Research and Applications 18 (2010) 432–452.
- [13] I. Oja, M. Nanu, A. Katerski, M. Krunks, A. Mere, J. Raudoja, A. Goossens, Thin Solid Films 480-481 (2005) 82-86.
- [14] M. Krunks, O. Kijatkina, A. Mere, T. Varema, I. Oja, V. Mikli, Solar Energy Materials and Solar Cells 87 (2005) 207–214.
- [15] A. Katerski, A. Mere, V. Kazlauskiene, J. Miskinis, A. Saar, L. Matisen, A. Kikas, M. Krunks, Thin Solid Films 516 (2008) 7110–7115.
- [16] C. Camus, N.A. Allsop, S.E. Gledhill, W. Bohne, J. Röhrich, I. Lauermann, M.C. Lux-Steiner, C.H. Fischer, Thin Solid Films 516 (2008) 7026–7030.

- [17] S. Nakamura, A. Yamamoto, Solar Energy Materials and Solar Cells 49 (1997) 415–421.
- [18] B. Asenjo, A.M. Chaparro, M.T. Gutiérrez, J. Herrero, Thin Solid Films 511–512 (2006) 117–120.
- [19] S. Nakamura, A. Yamamoto, Solar Energy Materials and Solar Cells 75 (2003) 81–86.
- [20] C.D. Lokhande, G. Hodes, Solar Cells 21 (1987) 215-224.
- [21] J. Herrero, J. Ortega, Solar Energy Materials and Solar Cells 20 (1990) 53-65.
- [22] A. Antony, A.S. Asha, R. Yoosuf, R. Manoj, M.K. Jayaraj, Solar Energy Materials and Solar Cells 81 (2004) 407-417.
- [23] R.P. Wijesundera, W. Siripala, Solar Energy Materials and Solar Cells 81 (2004) 147-154.
- [24] D. Lincot, J.F. Guillemoles, S. Taunier, D. Guimard, J. Sicx-Kurdi, A. Chaumont, O. Roussel, O. Ramdani, C. Hubert, J.P. Fauvarque, N. Bodereau, L. Parissi, P. Panheleux, P. Fanouillere, N. Naghavi, P.P. Grand, M. Benfarah, P. Mogensen, O. Kerrec, Solar Energy 77 (2004) 725–737.
- [25] Y. Onuma, K. Takeuchi, S. Ichikawa, Y. Suzuki, R. Fukasawa, D. Matono, K. Nakamura, M. Nakazawa, K. Takei, Solar Energy 80 (2006) 132–138.
- [26] S.M. Lee, S. Ikeda, T. Yagi, T. Harada, A. Ennaoui, M. Matsumura, Physical Chemistry Chemical Physics 13 (2011) 6662–6669.
- [27] C. Broussillou, M. Andrieux, M. Herbst-Ghysel, M. Jeandin, J.S. Jaime-Ferre, S. Bodnar, E. Morin, Solar Energy Materials and Solar Cells 95 (2011) S13-S17.
- [28] R.C. Valderrama, M. Miranda-Hernández, P.J. Sebastian, A.L. Ocampo, Electrochimica Acta 53 (2008) 3714–3721.
- [29] Q. Huang, K. Reuter, S. Amhed, L. Deligianni, L.T. Romankiw, S. Jaime, P.-P. Grand, V. Charrierb, Journal of the Electrochemical Society 158 (2011) D57–D61.
- [30] P.P. Prosini, M.L. Addonizio, A. Antonaia, Thin Solid Films 298 (1997) 191-196.

- [31] B.M. Basol, S. Aksu, J. Wang, U.S. Patent 20090283415 (2009).
- [32] S. Canegallo, V. Demeneopoulos, L.P. Bicelli, G. Serravalle, Journal of Alloys and Compounds 228 (1995) 23–30.
- [33] S.M. Lee, S. Ikeda, T. Harada, M. Matsumura, Journal of Non-Crystalline Solids, http://dx.doi.org/10.1016/j.jnoncrysol.2011.12.043.
- [34] S. Ikeda, T. Nakamura, S.M. Lee, T. Yagi, T. Harada, T. Minegishi, M. Matsumura, ChemSusChem 4 (2011) 262–268.
- [35] J.J. Scragg, P.J. Dale, L.M. Peter, G. Zoppi, I. Fobes, Physica Status Solidi (b) 245 (2008) 1772–1778.
- [36] These  $\alpha$  values were determined by measuring photoabsorption of the 100nm-thick CIS film deposited on a fluorine-doped tin oxide (FTO)-coated glass substrate using a spray technique.
- [37] P.L. Dale, Peter in Photoelectrochemical Materials and Energy Conversion Processes, Wiley-VCH, Weinheim, 2010.
- [38] L.M. Peter, Chemical Reviews 90 (1990) 753-769.
- [39] J. Li, R. Peat, L.M. Peter, Journal of Electroanalytical Chemistry 165 (1984) 41–59.
   [40] S. Ikeda, R. Kamai, T. Yagi, M. Matsumura, Journal of the Electrochemical Society
- 157 (2010) B99–B103.
  [41] T. Minemoto, T. Matsui, H. Takakura, Y. Hamakawa, T. Negami, Y. Hashimoto, T. Uenoyama, M. Kitagawa, Solar Energy Materials and Solar Cells 67 (2001)
- 83–88. [42] S.S. Schmidt, D. Abou-Ras, T. Unold, T. Eisenbarth, H. Wilhelm, Journal of Applied Physics 110 (2011) 064515.
- [43] R. Klenk, Thin solid films 387 (2001) 135-140.
- [44] M. Turcu, U. Rau, Thin Solid Films 432 (2003) 158-162.
- [45] B.J. Stanbery, Critical Reviews in Solid State and Materials Sciences 27 (2002) 45.
- [46] H.J. Hovel, Solar Cells, Academic Press, New York, 1975.