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Effect of potentials and electric charges for copper and indium depositions to the photocurrent responses of CuInS₂ thin films fabricated by stack electrodeposition followed by sulfurization

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Abstract. Effect of potentials and electric charges of copper and indium depositions to the photocurrent responses of CuInS₂ thin film fabricated by electrodeposition followed by sulfurization were investigated. The characterization and elemental compositions of as-deposited Cu/In and CuInS₂ thin films used μ -RD and EDAX. Photocurrent responses of the obtained CuInS₂ thin films were analyzed by linear sweep voltammetry (LSV) in europium solution under chopped irradiation. Photocurrent responses showed that fabricated CuInS₂ thin films had *p*-type photoresponses. Indium deposition on copper was influenced by copper morphology resulted by a certain potential deposition. Increasing potential of indium deposition on copper and electric charge of copper deposition reduced photocurrent for the former but did not change photocurrent of CuInS₂ for the latter.

1. Introduction

Chalcopyrite of copper indium sulfide (CuInS₂) has been used as a photocathode in the research of photoelectrochemical water splitting to produce H₂[1,2]. Since this ternary semiconductor compound has optimal band gap value for sunlight radiation (1.5 eV) [3], large absorption coefficient of 3×10^5 cm⁻¹ below 1000 nm [4] assures absorption of the entire incident photon flux in an absorber layer as thin as a few microns. Ideal absorber of CuInS₂ was prepared by stack deposition of Cu and In metallic layers on Mo glass substrate by vacuum methods such sputtering and evaporation [5,6], then the film was sulfurized using H₂S gas or elemental sulfur [7,8]. However, the methods need high cost for the equipment [9].

Electrodeposition is one of the promising technologies for fabrication of low-cost photovoltaic absorber films because of the low-cost equipment, scalability of large scale, and good control over film composition and morphology. CuInS₂ film fabricated by stack electrodeposition of Cu and In bilayer then followed by sulfurization has been applied as the most usual process [10-13]. However, for deposition of Cu and In on Mo glass substrate is very challenging due to difficulty of indium to deposit on copper layer. In this study, therefore, we examined fabrication of a CuInS₂ film by stack electrodeposition from a separate solution of copper and indium containing electrolytes. Effects of applied potentials on film compositions and morphologies were studied in detail. In addition, we



1 attempted to fabricate ternary CuInS_2 films by sulfurization of the as-electrodeposited film; electronic property of the thus-obtained films was also examined by using photo electrochemical measurement.

2 Experiment Methods

Material synthesis

Electrodeposition was carried out potentiostatically in a vertical three-electrode setup consisting of an Ag/AgCl as reference electrode, a Pt-sheet as counter electrode, and a Mo-coated glass substrate (Mo/glass) as a working electrode. Before the deposition, the Mo/glass substrate was pre-cleaned by sonication in acetone. The working electrode area was 0.7 cm^2 . The distance of the working electrode and counter electrode was kept constant at about 2 cm. The copper ion electrolyte used consisted of 50 mM CuSO_4 , 150 mM trisodium citrate, and 242 mM citric acid. The pH was adjusted 2.4 using H_2SO_4 . Indium electrolyte solution consisted of 30 mM InCl_3 , 242 mM citric acid, and 36 mM trisodium citrate. Electrodeposition was performed by scan potential from 0 to -1500 mV (vs. Ag/AgCl) for both copper and indium, separately. Then for copper, deposition was carried out at fixed potentials of -200 and -400 mV, while for indium the potentials were -760, -850 and -980 mV with electric charges of 730 mC and 840 mC for copper and indium deposition, respectively. The electric charge was changed for copper and indium depositions as stated in the discussion. The electrodeposition was done at room temperature without stirring using a Hokuto Denko HSV-110 potentiostat-galvanostat. The temperature of all depositions solutions was kept at $24 \pm 1 \text{ }^\circ\text{C}$ by immersion in a thermostated water bath. The as-deposited film was finally subjected to sulfurization at temperature of $560 \text{ }^\circ\text{C}$ under H_2S (5% in Ar) flow for 10 min. The film, then, was etched using KCN to remove Cu_xO [14-16].

Characterizations and photocurrent measurement

Elemental compositions of thus-obtained films were determined using a Hitachi TM3000 scanning electron microscope (SEM) equipped with a Swift ED3000 energy dispersive X-ray spectrometer (EDX). Crystal structures were measured by X-ray diffraction (XRD) analysis using Rigaku Mini Flex X-ray diffractometer (CuK α , Ni filter). Surface and cross-sectional morphologies of the films after sulfurization were examined using a Hitachi S-5000 FEG field emission scanning electron microscope (FE-SEM). Photoelectrochemical measurements were carried out using a three-electrode cell in 0.2 M $\text{Eu}(\text{NO}_3)_3$ electrolyte. A Pt wire and an Ag/AgCl electrode in saturated KCl served as the counter electrode and reference electrode, respectively, and Hokuto Denko HB-151 potentiostat-galvanostat was employed to obtain linear sweep voltammograms.

3. Results and discussion

Preparation of semiconductor of CuInS_2 by stack electrodeposition of the precursor was done by scanning the voltage applied, and the voltammogram of copper and indium deposition can be seen in Figure 1. Figure 1a shows that the valley of reduction potential of copper deposition is around -117 mV, while from Figure 1b for indium is around -814 mV. Therefore for deposition, we used -200 and -760 mV. The more negative potential we used caused the more hydrogen evolution, and this will reduce the electrodeposition efficiency.

Effect of the more negative potential (-400 mV) causes copper that deposited on molybdenum has dark color compared to the potential of -200 mV with a white red color. Besides that, the indium will be difficult to be deposited on the more negative copper deposited on molybdenum. Meanwhile, indium deposition on the copper layer is done at the potential of -200 mV of copper deposition.

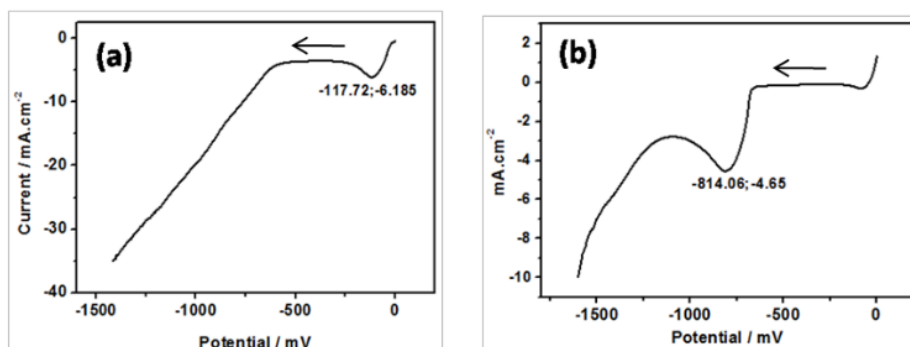


Figure 1. Voltammogram profiles of copper (a) and indium (b) depositions.

Copper deposition at different potentials is also characterized using SEM and XRD as shown in Figure 2 and 3, respectively. Surface SEM images show copper deposited at -200 mV produced bigger grains than deposited at -400 mV (Figure 2). While, from XRD spectra we can see different patterns of XRD of the copper deposited at -200 mV and -400 mV (vs. Ag/AgCl) as shown in Figure 3 that is the appearance of CuO pattern at 35° for copper deposited at -400 mV, this is also supported with the dark deposition of copper. It seems the crystal orientation of copper deposited -200 mV is favor for indium deposition.

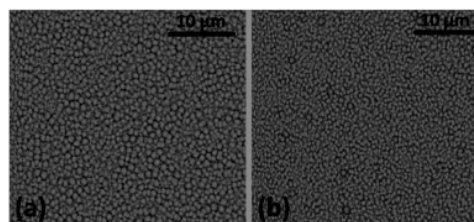


Figure 2. SEM images of Cu depositions at potentials of (a) -200 mV and (b) -400 mV.

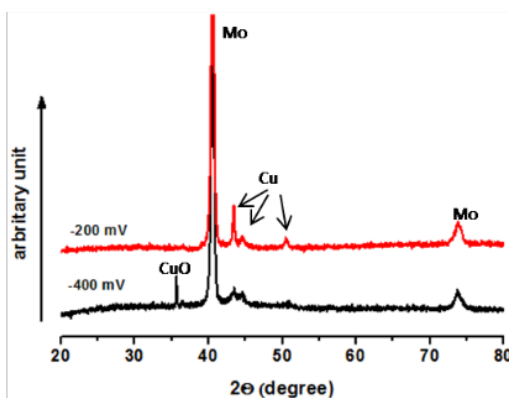


Figure 3. XRD-patterns of copper at different deposited potentials.

Evaluation of as-deposited Cu/In (deposited at -200 mV and -760mV (*vs.* Ag/AgCl) for copper and indium, respectively) using SEM, and EDAX are shown in Figure 4 and Table 1. Surface SEM image of the film shows the porous deposition of indium on copper layer (meaning the indium did not cover completely the surface of copper). Besides that indium did not cover homogeneously on the thin copper layer (as shown from cross section of as-deposited Cu/In SEM image). Elemental composition of as-deposited Cu/In can be seen in Table 1.

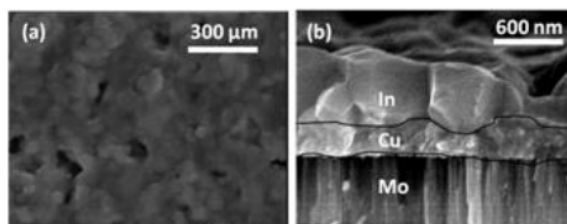


Figure 4. SEM images of Cu/In deposited at -200 mV and -760mV (*Vs.* Ag/AgCl) for copper and indium, respectively.

Table 1. Elemental composition of as-deposited Cu/In

Metal	Composition [%]
Copper	41.087
Indium	58.913

Sulfurization of as-deposited Cu/In (deposited at -200 mV and -760 mV (*vs.* Ag/AgCl) for copper and indium, respectively) produced CuInS₂ and the chalcopyrite properties appear after being etched using KCN as impurities remover in the semiconductor as confirmed at Table 2. However, the impurities were undetected from XRD pattern since the patterns are similar with CuInS₂ after etched with KCN (Figure 5).

SEM image shows the big grain of CuInS₂ with porous appearance. Cross section image of the film seen that the film was peeled off near the substrate in some part. And CuInS₂ has more than 1 μm thick as shown in Figure 6.

Table 2. Elemental composition of CuInS₂ before and after KCN etching

Metals	Percentage	
	Before KCN etching	After KCN etching
Copper	34.09	27.65
Indium	20.87	23.86
Sulfur	44.44	48.49

Analysis using XRD of as deposited Cu/In (Figure 3) appears the peaks of 43.4° and 50.5° as well as peaks of 34.5° and 43.1° correspond to copper and Cu/In, respectively. XRD patterns of CuInS_2 in Figure 6 affirm the chalcopyrite properties [17], and the sulfurization completely converted as-deposited Cu/In become CuInS_2 (written CIS in the figure) as shown the different pattern of the both.

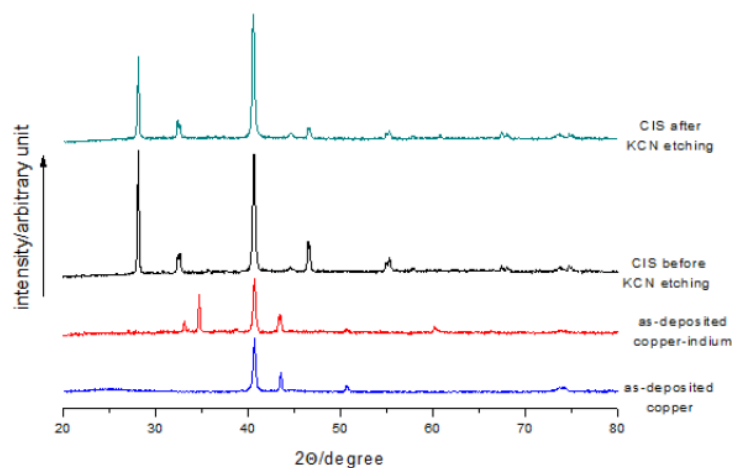


Figure 5. XRD patterns of as-deposited copper and Cu/In as well as CuInS_2 before and after etched using KCN.

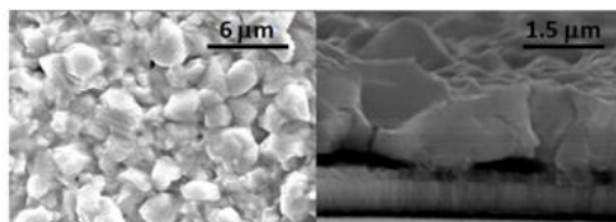


Figure 6. SEM images of CuInS_2 after etched using KCN.

The obtained CuInS_2 film, then, was tested for its photocurrent properties using europium solution under chopped illumination as shown in Figures 7 and 8. Figure 7 shows that the increase of more negative potential for indium deposition reduced the photocurrent of CuInS_2 film, this is due to the lower indium deposited on copper as confirmed by hydrogen appearance on the working cathode. As our previous work [18], we obtained the higher photocurrent of CuInS_2 using close the plateau of indium deposition, namely 760 mV. Meanwhile by increasing the electric charge (as shown in Figure 8) of copper deposition from 730 mC to 1 C did not change significantly the photocurrent of CuInS_2 thin film (indium deposition was kept constant at 840 mC). This can be the elemental composition of indium was quite enough to react with copper to form CuInS_2 semiconductor. When the electric charge was made double for both copper and indium deposition, we got the thicker film with lower photocurrent.

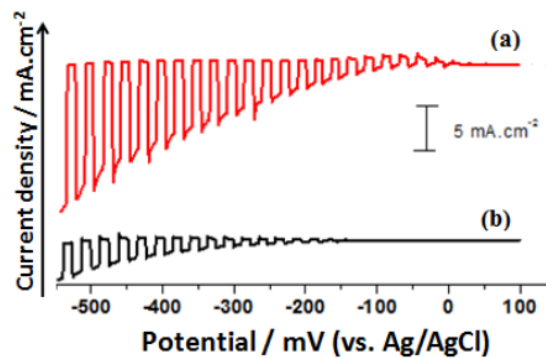


Figure 7. linear sweep voltammograms of CuInS_2 films (when indium was deposited using potentials of (a) -850 and (b) -980 mV under chopped light illumination in a 0.2 M $\text{Eu}(\text{NO}_3)_3$ electrolyte.

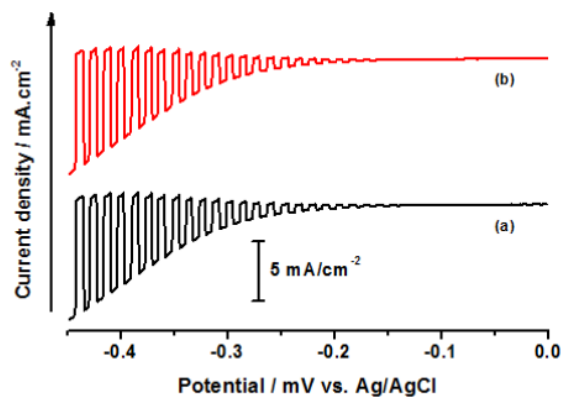


Figure 8. linear sweep voltammograms of CuInS_2 film (when coppers were deposited using electric charges of (a) 730 and (b) 1000 mC, respectively, under chopped light illumination in a 0.2 M $\text{Eu}(\text{NO}_3)_3$ electrolyte.

4. Conclusion

In the present study, Effect of potentials and electric charges of copper and indium depositions to the photocurrent responses of CuInS_2 thin film fabricated by electrodeposition followed by sulfurization were examined. Deposition of the desired copper and indium films was achieved by fixing appropriate applied potentials and electric charges, so that CuInS_2 with high photocurrent was obtained. Further works, especially work focused on obtaining highly crystalline CuInS_2 films having relatively high onset potential and photocurrent, which are believed to be optimum for photoelectrochemical water splitting to produce H_2 , are now in progress.

Acknowledgement

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