ANNEALING TEMPERATURE AND COCATALYST EFFECTS TO THE PHOTOELECTROCHEMICAL PROPERTY OF CuInS₂ THIN FILM SEMICONDUCTOR

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ABSTRACT

Thin film of CuInS₂ semiconductor had been synthesized by copper and indium stack electrodepositions on a molybdenum glass substrate and followed by sulfurization at varied annealing temperatures of 600-800 °C. CuInS₂ thin film was characterized by using XRD, Raman, and SEM. Then on the CuInS₂ was deposited Pt with various deposition times and its photocurrent property was observed. Finally, Pt or Rh cocatalyst deposited on In₂S₃-CuInS₂ was also measured its photoelectrochemical property. XRD, Raman, and SEM data showed CuInS₂ had a different character with varied annealing temperatures. An annealing temperature of 680 °C gave a maximum photocurrent of CuInS₂ as a photocathode. The introduction of cocatalysts increased the photocurrent, even for Rh cocatalyst gave a better-applied bias photon-to-current efficiency than Pt.

Keywords: Photocathode, CuInS₂, Cocatalyst, Photocurrent.

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INTRODUCTION

Photoelectrochemical (PEC) water splitting to produce hydrogen gas (H₂) by using sunlight is hoped to be an ideal and environmentally clean technology to replace fossil fuel sources which tend to reduce in the short years. This idea motivates the scientific community to find various materials and strategies for that purpose. Fujishima *et al.* as the pioneer of PEC water splitting applied photoanode of TiO₂ irradiated by using UV light.¹ The finding motivated researchers to find out various types of semiconductors and configurations of PEC devices to improve the efficiency of water reduction to produce hydrogen gas (H₂).²⁻⁷

Single absorber with a wide bandgap gives a low efficiency of PEC water splitting because it only works at UV light, therefore to improve the efficiency by harvesting all sunlight irradiation regions dual absorbers seem more promising. They consist of photoanode and photocathode electrodes that function as water oxidation and reduction, respectively. With this dual absorber system, researchers can be more flexible and optimal to focus on each electrode, so that it is possible to obtain a real splitting of water without bias by irradiation using sunlight to the absorbers.

Considering the absorber as the cathode part, the materials of Cu-based chalcopyrite as a *p*-type semiconductor are promising candidate absorbers for producing H₂ evolution efficiently.⁸⁻¹³ The compound of CuInS₂ is one of the most important chalcopyrite because it has an optimal value of the bandgap and high absorption coefficient, namely 1.5 eV and 10⁴ cm⁻¹, respectively, that allowing it to utilize sunlight efficiently.¹⁴ Moreover, low-cost electrodeposition and annealing methods of thin-film

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fabrication techniques enable to prepare CuInS₂ photoelectrodes with high structural and optical quality.¹⁵⁻¹⁸ Surface modification of CuInS₂ using buffer layer of *n*-type and platinum introduction enhances the cathodic photocurrent and it is very important for a better separation of electrons and holes generated by illumination.¹⁹ Platinum is the best cocatalyst until now to perform hydrogen evolution reaction by facilitating interfacial charge transfer reactions²⁰. Meanwhile, for water reduction, the semiconductor surfaces as electrodes have no especially catalytic property due to their high photogenerated carrier recombination. As it is usually applied widely in solar cells by fabrication *p* and *n* types of semiconductors of Cu-based chalcopyrite (*p-n* junctions) the covering of *n*-type of buffer layer on photo absorbers increases the photocurrent of the photocathode.²¹⁻²⁴ In this study, we investigated the effect of annealing temperatures of CuInS₂ thin film, and insertion of cocatalyst of Pt or Rh on the surface of photocathode of In₂S₃ covered CuInS₂ to improve its photoelectrochemical property since limited previous works discussed these cases. Their works mainly correlated to the temperature annealing effect of CuInS₂ on the structural and morphological as well as optical properties.^{25,26}

EXPERIMENTAL

Materials and Instrumentations

The chemicals used were CuSO₄, InCl₃, trisodium citrate, citric acid, acetone, KCN, In₂(SO₄)₃, thioacetamide, CH₃COOH, H₂PtCl₆, RhCl₃, Na₂SO₄, Eu(NO₃)₃, NaH₂PO₄. All chemicals were bought from *Merck* and used without purification. Molybdenum glasses were purchased from Geomatec Ltd. Japan. For annealing and drying the Cu/In film used H₂S (5%) and N₂ gases, respectively.

Potentiostat (Hokuto Dento 110) was used for electrodeposition of copper, indium, platinum and rhodium. X-ray diffraction (XRD) was performed for analysis of crystalline structures of the CuInS₂ film using *PANalytical X Pert³ Powder* X-ray diffractometer (Cu K α , Ni filter). The CuInS₂ thin film's morphology was analyzed by using a scanning electron microscope (SEM) JSM-6510LA Analytical at an acceleration voltage of 20 kV. Raman analyses were obtained by using Raman Spectrophotometer (Jasco NRC 3100 Laser) with an excitation laser at a wavelength of 532 nm. Photocurrent responses and PEC measurements of bare and modified CuInS₂ used potentiostat coupled with digital function generator at 0.3 Hz and Shutter Controller.

Electrodeposition of Cu/In on Molybdenum Glass

The electrodeposition was carried out from copper then continued with indium electrolyte solutions successively with Ag/AgCl, Pt-wire, and a Mo-covered glass substrate (0.7 cm x 1.0 cm) as a reference, counter and working electrodes, respectively. Copper electrolyte pH 2.38 contained 0.05M CuSO₄, 0.15M trisodium citrate, and 0.242M citric acid. While indium electrolyte contained 0.03M InCl₃, 0.242M citric acid, and 0.036M trisodium citrate. The electrodepositions were run for 7 and 15 min for copper and indium using potentiostat at potentials of -0.2 and -0.78 V, respectively.

Effect of Annealing Temperature of CuInS₂

As deposited Cu-In was converted to CuInS₂ by pre-annealing for 30 min at a temperature of 160 °C in Ar gas with flow rate at 200 mL/min and annealing for 10 min under 200 mL/min of H₂S (5% H₂S) flow in a glass tube furnace. The annealing temperature was varied at a temperature from 600 until 800 °C. Then the CuInS₂ was immersed in KCN (10%) for 2 min to remove excess of Cu_xS. Effect of annealing temperature of CuInS₂ was observed by photocurrent response measurements used potentiostat coupled with digital function generator at 0.3 Hz and Shutter Controller. Three electrodes containing Ag/AgCl electrode, Pt counter electrode and CuInS₂ as working electrode were immersed in 0.2M Eu(NO₃)₃ solution. The measurement was run by chopped 1.5 AM light radiation to the working electrode with a sweep potential from 0 until -0.45V and a scan rate of 10 mV/s. Analysis of Raman, XRD and SEM were applied to characterize the effect of varying temperatures on synthesized CuInS₂.

Effect of Pt Cocatalyst Deposition

Pt electrodeposition on bare-CuInS₂ films was done using 20 mL electrolyte consisting 1mM H₂PtCl₆ and 0.1M Na₂SO₄ in cylindric flask with a window. Then into the flask was inserted bare-CuInS₂

photocathode, Pt, and Ag/AgCl as working, counter, and reference electrodes, respectively. Pt was photoelectrodeposited on the working electrode at various deposition times using potentiostat under illumination. Photocurrent response was measured using a similar procedure as above.

Effect of Type of Cocatalysts

Before deposition of cocatalysts, bare-CuInS₂ film was covered with In₂S₃ by immersed in an electrolyte containing 0.025M indium sulfate, 100 mM thiacetamide and 100 mM acetic acid at 65 °C for 15 min. Then Pt or Rh was deposited on modified CuInS₂ with a similar procedure as above with concentration 1mM for 10 s. Photoelectrochemical properties were performed in 0.2 M NaH₂PO₄ solution using a similar instrument and parameter as photocurrent response measurement. APBE (applied bias photon-to-current efficiency) was evaluated using equation:

$$\text{APBE (\%)} = J \times V_b \times 100 / P_{\text{AM1.5}}$$

Where J is photocurrent (mA/cm²), V_b is bias voltage (RHE scale), and P_{AM1.5} is 1.5AM simulated radiation (100 mW/cm²). While RHE is calculated as the following, $\text{RHE} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + 0.199$.

RESULTS AND DISCUSSION

Effect of Annealing Temperature of CuInS₂

Preparation of semiconductors of CuInS₂ by successive electrodeposition of Cu and In of the precursor was conducted by annealing as-deposited Cu/In in H₂S gas at a temperature of 600 until 800 °C. The obtained CuInS₂ then were examined their photocurrent responses in 0.2 M europium solution (as electron scavenging) with chopped illumination and the results are depicted in Fig.-1. The figure can be seen the maximum photocurrent around 12.2 mA/cm² at a potential of -0.4V for CuInS₂ annealed at 680 °C with a good dark current. There is an anomaly in the results of the photocurrent response at temperatures of 620 and 640 °C. However, the photocurrent response has a trend to be optimum at 680 °C and becomes decrease after that temperature; those are 5.8 and 5.2 mA/cm² at annealing temperatures of 750 and 800°C, respectively (Tabel-1). CuInS₂ annealed at 700 to 800 °C gave a bad dark current, since the dark current not flat. The good absorber semiconductor should have zero current when there is no light (at dark).

Fig.-1: Current-potential Curves of CuInS₂ measured using Potentiostat in Europium Solution under Chopped 1.5AM Simulated Radiation using Three-electrode systems.

Tabel-1: Photocurrent Response of CuInS₂ after Annealing at Varied Temperatures

Annealing Temperature (°C)	600	620	640	660	680	700	750	800
Photocurrent at Potential of -0.4 V (vs. Ag/AgCl) (mA/cm ²)	-8.1	-5.0	-3.8	-7.9	-12.2	-9.7	-5.8	-5.2

Figure-2 shows are typical CuInS₂ spectra at different annealing temperatures using Raman spectrophotometer. Raman shift at ca. 300 cm⁻¹ is a typical peak for CuInS₂ and no other peaks appear for annealing temperatures until 680 °C. Whilst at annealing temperatures of 700 until 800 °C beside the peak of CuInS₂, there are other peaks of molybdenum element coming from molybdenum glass substrate used because the molybdenum was evaporated and deposited at the surface of CuInS₂ thin film when subjected to the temperatures. Therefore, it covered the surface of CuInS₂ confirmed by the low-intensity peaks of CuInS₂ thin films annealed at temperatures of 700, 750, 800 °C. The molybdenum has Raman shifts ca.321.8, 407.4, 453.4 cm⁻¹.

Fig.-2: CuInS₂ Raman Spectra annealed at Various Temperatures

The XRD spectra of CuInS₂ obtained from various annealing temperatures are shown in Fig.-3. The figure shows that at 2θ of 40.8° is the peak from molybdenum. While diffraction peaks at ca. 28.2, 46.8, and 55.4° are corresponding to the main crystalline chalcopyrite CuInS₂ phase. The values are almost close to the work of Bini *et al.*²⁷

Fig.-3: XRD of CuInS₂ Obtained from Different Annealing Temperatures

Thin-film of CuInS₂ grain size was evaluated using formula of Debye-Scherrer, namely, $D = 0.9 \lambda / \beta \cos\theta$. The values of D, λ , β , and θ are the diameter of the crystallites forming the film, wavelength of the CuK α line, FWHM and Bragg angle, respectively. The average grain sizes obtained from all peaks of CuInS₂ are in the range of 23 and 38 nm (Fig.-4). As the temperature increases, the grain size improves until temperature 640 °C with the highest grain size of 38.36 nm and after that, the grain size becomes decreases to 32.48 nm. As it is seen from Raman curve at higher annealing temperature (>700 °C) was not merely CuInS₂ present in the thin film. Since the CuInS₂ thin films prepared is almost pure, increasing temperature is effective until 640 °C, this is also confirmed by previous research that showed annealing temperature of CuInS₂ until the temperature of 550 °C.²⁸

Figure-5 shows SEM of a thin film of CuInS₂ annealed at the temperatures of 600, 640, and 750 °C as a representation for three areas that have different grain sizes as shown in Fig.-4. The SEM shows that for CuInS₂ annealed at 600 °C has a porous property and small grain size, meanwhile the CuInS₂ annealed at

640 °C has a bigger grain size and also it looks like the film became melt. Although the decrease of grain size did not appear at an annealing temperature of 750 °C, the melted-like was disappeared. This can be due to the presence of molybdenum covered on its surface as confirmed by Raman measurement.

Fig.-4: Average Grain Size of a Thin Film of CuInS₂ at Various Annealing Temperatures

Fig.-5: SEM of CuInS₂ Annealed at Temperatures of 600, 640, and 750 °C

Effect of Pt cocatalyst Deposition

Platinum is a cocatalyst for hydrogen evolution reaction since it can bind with hydrogen ion to form ideal bond strength of Pt-H that can facilitate adsorption process and reduction of hydrogen ion and to release H₂ easily when reduction process is complete.²⁰ Figure-6 shows the deposition of Pt improves the photocurrent and onset potential compared with bare-CuInS₂. The photocurrent increases from 1.5 to 5 mA/cm² for bare and Pt deposited CuInS₂, respectively. While the onset potential gave more positive potential for Pt deposited CuInS₂ than bare-CuInS₂. However, the increase of deposition times (from 20 s until 1 h) has no significant effect on photocurrent as well as onset potential of Pt-CuInS₂.

Fig.-6: Effect of Platinum Deposition Times on CuInS₂ to the Curves of Current-potential of Pt-CuInS₂ Photocathode measured in 0.1 M Na₂SO₄ at pH 9 under Chopped 1.5AM Simulated Radiation

Effect of Type of Cocatalyst

Effect of type of cocatalyst was evaluated using Rh as replacement of Pt. Since Pt has a work function a relatively large ca. 5.65 eV,²⁹ the formation of Schottky-type potential barrier would be possible that resists the transfer of electron. Therefore, Pt can be replaced by Rh as a candidate to reduce the potential barrier because of its relatively small work function (4.98 eV),²⁹ possible depositions by a photoelectron chemical method similar to that employed for the platinum deposition, and relatively low overpotential for water reduction comparable to that of Pt.^{30,31} Figure-7a shows typical current and potential scans of Pt and Rh covered $\text{In}_2\text{S}_3/\text{CuInS}_2$ electrodes, respectively. The result shows appreciable improvement of photocurrent and also the onset potential achieved by using Rh catalyst for the $\text{In}_2\text{S}_3/\text{CuInS}_2$ electrode and improving the ABPE more than 2 % for Rh catalyst, as shown in Fig.-7b. Since there is no significant improvement when the Rh catalyst was used instead of the Pt catalyst for the $\text{CdS}/\text{CuInS}_2$ electrode system, the use of Rh should work well by a combination with In_2S_3 but not for CdS having a relatively negative conduction band minimum (CBM).³² Figure-8 shows the energy diagram of $\text{In}_2\text{S}_3/\text{CuInS}_2$, Rh and Pt. The absolute and the electrochemical scales are given on the right side.

Fig.-7: (a) Current-potential Curves of Pt and Rh covered $\text{In}_2\text{S}_3/\text{CuInS}_2$ Photocathodes, respectively, in a Solution of 0.2 M NaH_2PO_4 at pH 6 with Chopped AM 1.5 Simulated Irradiation. (b) ABPE of Pt and Rh covered $\text{In}_2\text{S}_3/\text{CuInS}_2$ Photocathode, respectively.

Fig.-8: Energy Diagram of $\text{In}_2\text{S}_3/\text{CuInS}_2$, Rh and Pt. The Absolute and the Electrochemical Scales are given on the Right Side.

CONCLUSION

CuInS_2 thin film had an optimum photocurrent response value of 12.2 mA/cm^2 when it was annealed at 680°C . Deposition of platinum on CuInS_2 improved the photocurrent compared to bare CuInS_2 . However, increasing times of Pt depositions had no significant effect on photoelectrochemical properties of the Pt- CuInS_2 photocathodes. Due to the relatively high CBM of the In_2S_3 photocathode layer, direct deposition of conventional Pt catalysts was found to be not optimal due to the generation of a large Schottky barrier; instead, the use of Rh was beneficial for this system, though it is still not sufficiently improved.

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