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2013

Sun, J., Batabyal, S. K., Tran, P. D., & Wong, L. H. (2014). Electrodeposition of single phase CuInSe₂ for solar energy harvesting: Role of different acidic additives. *Journal of Alloys and Compounds*, 591, 127-131.

<https://hdl.handle.net/10356/104515>

<https://doi.org/10.1016/j.jallcom.2013.12.178>

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Electrodeposition of single phase CuInSe₂ for solar energy harvesting: role of different acidic additives

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Abstract:

Single phase CuInSe₂ (CIS) absorber material is required for producing high quality thin film solar cells, as the presence of impurity Cu_{2-x}Se leads to short circuit of the cells. Traditionally, the deposition of single phase CIS requires the use of a suitable chelating agent to shift the Cu²⁺/Cu redox couple towards the redox potential of the In³⁺/In couple, and also an acid to adjust the pH of deposition bath around 2. We propose a novel idea of using suitable acids that could concurrently also serve as the chelating agent. Oxalic acid, acetic acid and hydrochloric acid were investigated on their ability to serve this dual function. We found that oxalic acid is the most promising additive because the CIS film deposited was densest and yielded the highest photocurrent.

Keywords: Thin film solar cells, Single phase, Electrodeposition, Cu-complex, CIGS

1. Introduction

CuInSe₂ (CIS) is a promising absorber material for thin film solar cell application due to its high absorption coefficient ($\sim 10^5 \text{cm}^{-1}$), appropriate band gap and long term optoelectronic stability[1, 2]. CIS films can be fabricated by vacuum[3, 4] or non-vacuum [1, 5] based methods. Non-vacuum fabrication of thin film photovoltaic device provides an attractive cost saving opportunity that has generated a considerable amount of research interest [6, 7]. Of the various non-vacuum methods, electrodeposition is a highly attractive proposition for mass production of low cost CIS thin film solar cell [1, 2, 8, 9]. At present, the efficiency of cells produced by this method is reported to have achieved 15.9% by Nexcis(module efficiency of 12.2%)[2]. Other notable advantages of electrodeposition are lower equipment cost, higher deposition speed and less waste of chemicals as compared to vacuum methods[10].

Conventional deposition bath for one step electrodeposition of CIS thin film comprises Cu^{2+} , H_2SeO_3 and In^{3+} precursors in a strong acidic environment of pH 1.5-2[11, 12]. The acidic environment is usually created by the addition of strong acids. The conventional bath has a major problem. Significant difference in reduction potential of Cu^{2+}/Cu and In^{3+}/In redox couples in the bath results in higher deposition rate of Cu^0 compared with that of In^0 . Excess deposition of Cu^0 results in the formation of Cu_{2-x}Se impurity in the CIS film[13]. This Cu_{2-x}Se secondary phase is the path of low electrical resistance [10, 11] which decreases the power conversion efficiency of the CIS solar cells. Tendency to form the undesired Cu_{2-x}Se secondary phase can be reduced by shifting the reduction potential of the Cu^{2+}/Cu couple to more negative potential [12]. It is reported that adding additives that can chelate with Cu^{2+} is effective to shift the reduction potential [4-7]. Sodium citrate[14], tartaric acid[15], potassium thiocyanate[16], triethanolamine

[17] and sodium dodecyl sulfate[12] were studied for this purpose. It should be noted that in these studies, additional strong acids were required to maintain the pH around 1.5-2.

In this paper, we present a novel and direct way to employ simple organic acids as the chelating agent. This eliminates the need for addition of acids into the deposition bath since the acidic environment is already provided by the chelating agents. We investigated the ability of oxalic acid, acetic acid and hydrochloric acid for this dual role function. Oxalic and acetic acids are weak acids that form complexes and could act as chelating agents. Hydrochloric acid, on the other hand, is a strong acid. Strong acids do not form complexes and have no chelating properties. HCl serves as a control in the experiment. These organic acids were tested for their ability to prevent secondary phase formation in the CIS film. The CIS films were then tested for their photoelectrochemical properties by measurement of the photocurrent.

2. Experimental details

2.1 Electrodeposition of CIS thin films

All chemical compounds were purchased from Sigma Aldrich and used as received without any further purification. For our electrochemical experiments, a conventional three electrodes configuration was employed. This setup consists of a Pt mesh counter electrode, Ag/AgCl/KCl (3M) reference electrode, and freshly cleaned glassy carbon ($S = 0.071 \text{ cm}^2$) or clean fluorine doped tin oxide (FTO, $S = 1 \text{ cm}^2$) working electrode.

The composition of the deposition bath includes 4mM CuCl_2 , 8mM InCl_3 , and 8mM H_2SeO_3 in DI water. The initial pH of the deposition bath was adjusted to pH 2 using appropriate amount of HCl, acetic acid or oxalic acid. Linear sweep voltammograms were recorded on glassy carbon electrode for the deposition bath. Potential scan was performed in cathodic direction with a scan rate of 10 mV.s^{-1} . CIS film was deposited onto clean FTO electrode, with typical surface area of

1cm², at a fixed cathodic potential (between -0.6 and -1.0V vs. Ag/AgCl) for 20 minutes. The as-deposited CIS films were carefully rinsed under DI water and dried under a N₂ flux. Lastly, the films were annealed in N₂ at 350°C for 1.5 hours

2.2 Characterizations

The crystal structure and chemical composition of the deposited CIS films were characterized by thin-film XRD, field emission scanning electron microscope (FESEM), Raman spectroscopy and energy dispersive spectroscopy (EDS).

To investigate the photoelectrochemical properties of deposited CIS films, photocurrent generated by these films under white light irradiation (150W Halogen lamp) at applied bias of -0.4V vs. Ag/AgCl was measured. Light intensity reached CIS electrode was kept at 100mW.cm⁻². A pH 7 phosphate buffer electrolyte solution was employed. Details of experimental setup, sample preparation etc were described in our previous work[18].

3. Results and discussion

Figure 1 here

Linear sweep voltammetry was employed to investigate the electrochemical properties of the CIS deposition baths with different acid additives. Four reduction peaks were observed at -0.05V, -0.2V, -0.4V and -0.7 V (marked as A3, B3, C3 and D3 respectively) vs. Ag/AgCl (Fig.1, green curve) when HCl is used to adjust the pH in the deposition bath. The first two peaks (A3 & B3) can be attributed to one electron reduction of Cu²⁺ into Cu⁺ and subsequently Cu⁺ into Cu⁰. The peak around -0.4V vs. Ag/AgCl is attributed to the reduction of H₂SeO₃ into Se (peak C3) and the most negative peak at -0.7V (peak D3) is attributed to the reduction of In³⁺ into In (Four rectangular boxes in Fig.1 represent the four different reduction windows of Cu²⁺/Cu⁺, Cu⁺/Cu⁰,

In^{3+} /In and H_2SeO_3 / Se respectively). The use of weak organic acids (acetic or oxalic acid) as chelating agents in the bath resulted in a cathodic shift in the reduction potential of $\text{Cu}^{2+}/\text{Cu}^+$ and Cu^+/Cu^0 couples. This phenomenon was similar to the observation that has been reported for triethanolamine additive [17]. The reason for this cathodic shift is likely due to the chelating of Cu^{2+} with acetic or oxalic acid which reduces the electrochemical activities of Cu^{2+} . Of these two weak acids, acetic acid additive induced a larger cathodic shift for the reduction potential of the Cu^{2+}/Cu couple. The presence of acetic acid in the deposition bath also resulted in the cathodic shift for reduction of H_2SeO_3 and In^{3+} .

The exact mechanism of the electrodeposition of CIS thin film still remains debatable. However, currently, it is widely accepted that the deposition mechanism is a result of the combination of electrochemical and chemical reactions as described in the following equations 1-5 [19, 20]. The precursors (Cu^{2+} , In^{3+} and SeO_3^{2-}) are first individually reduced into their elemental forms. The elements then react, most likely via a solid-state chemical reaction, to yield the final product. The combination of products formed from the chemical reactions depends on the amount of Cu^{2+} which is reduced to Cu (equation1). In particular, when the amount of Cu^{2+} reduced is much more than that of In^{3+} reduced, a mixture of ternary phase CIS and binary phase Cu_{2-x}Se may be formed.

Total reaction:

The difference in reduction potential between Cu^{2+}/Cu and In^{3+}/In couples dictates the composition of deposited CIS film [13]. Narrower difference in potential results in the formation of CIS film which contains less secondary Cu_{2-x}Se phase. Such structure is desirable for solar cell applications. From Fig.1, the difference in reduction potential between $\text{Cu}^{2+}/\text{Cu}^0$ and $\text{In}^{3+}/\text{In}^0$ is 520mV for HCl, 460mV for acetic acid, but only 370 mV for the oxalic acid additive. This indicates that oxalic acid is better than HCl and acetic acid for single phase CIS film deposition.

The shifts in the reduction potential may have resulted from different dissociation properties of the three acids. Table 1 [21] shows the acidic dissociation constant of these three acids which were used as chelating agents in our CIS electrodeposition study. The pKa value of acetic acid is 4.79, which is much higher than the pH of the reaction (pH 2). The pKa value indicates that majority of acetic acid is in protonated form when added into deposition bath. In protonated forms, acetic acid does not have good chelating properties. On the other hand, oxalic acid has pKa₁ of 1.38. It means that in the CIS deposition bath (pH 2), oxalic acid exists predominantly in the monoanionic form $\text{COOH}^-\text{COO}^-$. This form of oxalic acid has strong chelating properties. While HCl is a strong acid that dissociates fully and exists completely in the protonated form, it has no chelating properties and is used as a control in this experiment.

Table 1 here

Fig.2a shows the XRD patterns of CIS deposited at -0.7V vs. Ag/AgCl for 20mins using different additives after annealing. From the XRD analysis, we observed oxalic acid additive resulted in single phase CIS (JCPDS 00-040-1487) film, while HCl and acetic acid additives

resulted in the formation of CIS film with Cu_7Se_4 (JCPDS 00-026-0557) secondary phase. At $2\theta=44^\circ$ (2 0 4) crystallographic plane of CIS, a “hump”, corresponding to a secondary phase was observed. Normalization of the data allows the comparison of the “hump” intensity as shown in Fig. 2b and Fig. 2c.

Figure 2 here

Rietveld refinement revealed that highly pure CIS film was achieved using oxalic acid while Cu_7Se_4 secondary phase was found to be 14.20% for the HCl case and up to 34.60% for the acetic acid case.

Figure 3 here

We further investigate the chemical composition of the deposited CIS films by Raman spectroscopy. Raman spectroscopy can reveal vibration signatures which indicate the presence of amorphous phases in CIS films. These amorphous phases cannot be detected by thin film XRD analysis. The Raman spectrum of the CIS film with oxalic acid in Fig.3(olive color) shows chalcopyrite CIS A1 and E vibration modes at 180cm^{-1} and 210cm^{-1} [22]. Raman spectra for CIS films deposited with HCl or acetic acid in the deposition bath revealed another strong peak at 262cm^{-1} , characteristic for A1 vibration mode of Cu-Se compound. This further confirms the presence of Cu-Se impurities in these films [22]. In addition, the intensity of the 262cm^{-1} peak is higher for the film deposited with HCl film as compared with the one deposited with acetic acid. This is consistent with the theory that acetic acid has better chelating properties compared to HCl.

Both Raman spectroscopy and XRD analysis reveal the absence of Cu-Se impurities in CIS films deposited when oxalic acid was used as precursor. There seems to be some discrepancy between the Raman and XRD data when comparing between acetic acid and HCl precursors. Raman spectroscopy revealed that Cu-Se impurities in CIS film deposited with HCl in the deposition bath is more than that deposited with acetic acid; while XRD data analysis showed that Cu-Se in film deposited with acetic acid is more than that obtained with HCl. This discrepancy between Cu-Se detected by these two analyses may be because of that XRD detects only the crystalline Cu-Se while Raman spectroscopy detects both the amorphous and crystalline Cu-Se. Hence, presence of HCl in the deposition bath results in lower amount of crystalline Cu-Se, but a higher amount of total Cu-Se (amorphous and crystalline) as compared to having acetic acid in the deposition bath. In summary, the film deposited with HCl acid has the highest percentage of Cu-Se impurities compared with that obtained with acetic acid, and the film obtained with oxalic acid is a single phase CIS and does not contain any Cu-Se. This result is consistent with our LSV data in Fig. 1; which shows the variations in difference of reduction potential (Dv) between $\text{Cu}^{2+}/\text{Cu}^0$ and $\text{In}^{3+}/\text{In}^0$ for three deposition bath. Dv for HCl is greater than the Dv for acetic acid, and Dv for acetic acid is greater than the Dv for oxalic acid.

Figure 4 here.

As shown in the Fig.4a, the addition of acetic acid yields plate-like morphology dispersed in granular background. EDX analysis shows that these plates are Cu-Se and the background matrix is CIS. These plate-like structures appear to be elongated in the horizontal axis compared to CIS. The film obtained with HCl additive (Fig.4b) seems to be very rough. Using oxalic acid as the additive resulted in deposition of denser film which contains larger CIS grain size (Fig.4c). While the stoichiometry (Cu:In:Se) for sample c(Fig.4c) 1.15:1:2, is the closest to 1:1:2(Table2).

Table2 here

Figure 5 here

Finally, photoelectrochemical current measurements were carried out to compare the photon harvesting ability of the films deposited with different acids[23]. Fig.5 shows that all obtained CIS films are p-type semiconductor which yields cathodic photocurrent under light excitation. The dark current of the CIS film formed with HCl in the deposition bath increases with time, indicating the chemical instability of the film. That might be due to the chemical and/or photochemical corrosion of Cu-Se amorphous phase. The photocurrent measured for the film deposited using oxalic acid additive in the deposition bath ($60 \mu\text{A}/\text{cm}^2$) is slightly higher than that obtained for the film grown with acetic acid additive in the deposition bath ($50 \mu\text{A}/\text{cm}^2$). Both films are stable under illumination condition. Therefore, in terms of photoelectrochemical properties, single phase CIS obtained with oxalic acid additive in the deposition bath gives the best performance.

4. Conclusions

Crystalline, single phase p-type CIS thin films have been successfully deposited by one-step electrodeposition at -0.7V vs Ag/AgCl using conventional deposition bath containing Cu^{2+} , H_2SeO_3 , In^{3+} precursors and oxalic acid as chelating agent. The use of acetic and hydrochloric acid as chelating agent in the deposition bath resulted in the CIS films with amorphous Cu-Se secondary phases, which is detrimental to the electrical behavior of CIS solar cell devices. This study demonstrated that the use of oxalic acid as a chelating agent in the deposition bath is the most effective to eliminate Cu-Se secondary phase from electrodeposited CIS film and also

resulted in the most compact and uniform morphology. It exhibits the best photo-response among all of the films under time dependent photocurrent measurement. Finally, this study suggests that oxalic acid has great potential to be an effective chelating agent in the deposition of single phase p-type CIS thin film for solar energy harvesting.

Acknowledgments

We thank the National Research Foundation of Singapore, Economic Development Board of Singapore, A*STAR SERC Printed Electronic Program (Grant No. 1021700143) and the Center for Artificial Photosynthesis, NTU for providing financial support.

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Figure and Table captions

Fig.1. Linear sweep voltammograms collected on FTO electrode for CIS deposition bath at pH 2 adjusted by different acids with scan rate: 10mV.s^{-1} . A,B,C,D represent the conversion of $\text{Cu}^{2+}/\text{Cu}^{+}$, $\text{Cu}^{+}/\text{Cu}^0$, In^{3+}/In and $\text{H}_2\text{SeO}_3/\text{Se}$ for oxalic acid(1), acetic acid(2), and HCl(3) respectively.

Fig.2. (a) XRD patterns of electrodeposited CIS films after annealing in N_2 at 350°C for 1.5 hours (Stars indicate the peaks from substrate); (b) magnification of the humps around (204) peak; (c) XRD data refinement according to the hump around (204) peak.

Fig.3. Raman spectra of CIS thin films added with three different acids.

Fig.4. SEM images of annealed CIS films deposited at -0.7V vs. Ag/AgCl : (a) with acetic acid; (b) with HCl acid; (c) with oxalic acid.

Fig.5. Photocurrent generated under white light illumination employing CIS films which were deposited with different acids, hold at -0.4V vs. Ag/AgCl in a pH 7 phosphate buffer solution.

Table 1: Structure and pKa value of different additives[21].

Table 2: Atomic ratio of Cu: In: Se for the CIS films deposited with different acidic additives.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Table 1.

Chelating agents	Structure	pKa
oxalic acid		pKa ₁ = 1.38, pKa ₂ = 4.28
acetic acid		pKa= 4.79
HCl	H ⁺ Cl ⁻	Strong acid, no pKa

Table 2.

Different acid additives	Cu :I n : Se
oxalic acid	1.15 : 1 : 2
acetic acid	1.23 : 1 : 1.96
HCl	1.71 : 1 : 2.3