

Effect of sulfamic acid as complexing agent on electrodeposition of CIGS absorber thin film

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Cyclic voltammetry (CV) studies of unitary Cu, Ga, In and Se systems, binary Cu-Se system, and quaternary Cu-In-Ga-Se have been carried out in the solutions with different concentration of sulfamic acid to understand the role of this acid as a complexing agent. Cu(InGa)Se₂ (CIGS) thin films were deposited on Mo/soda-lime glass substrates by electrodeposition in the same applied potential and the same electrolyte bath but different in concentration of sulfamic acid, from 0 mM to 40 mM. The composition of the films was determined by EDS. The crystalline structure and morphology of the films were characterized by XRD and SEM, respectively. The obtained results indicate that sulfamic acid with an appropriate concentration (about 20-30 mM) can inhibit the underpotential deposition of Cu-Se phases and the H⁺ reduction into H₂ which are considered as the undesired process. On the other hand, sulfamic acid can promote the reduction of Ga³⁺, consequently can increase the Ga concentration. The desired Cu(In_{0.70}Ga_{0.30})Se₂ stoichiometry was obtained in the films grown from solution which contains 20-30 mM sulfamic acid.

Key words: CIGS, Electrodeposition, Complexing agent, Thin film, Solar cell.

Introduction

Over the past decades, Cu(InGa)Se₂ has been considered as one of the most promising photovoltaic materials for developing low-cost and high-efficiency thin film solar cells because it has a large optical absorption coefficient ($5 \times 10^5 \text{ cm}^{-1}$) which results from the direct band gap [1-3]. The CIGS base-thin film solar cell has reached a conversion efficiency of 20.3% for laboratory-size devices fabricated from a physical vapor deposition process (PVD) [4]. There have been a number of low-cost processing methods for the growth of high quality CIGS absorber thin film including both physical and chemical techniques. Among these techniques, electrodeposition deserves special attention because it is economic, simple, and allows to deposit over large surface areas. Electrodeposition of high-quality CIGS absorber for thin film solar cell has become the focus of many research groups in the field of solar energy. A conversion efficient as high as 15.4% has been achieved in the devices with CIGS film grown by electrodeposition and adjusted the composition by PVD [5]. There are two different electrochemical approaches to form CIGS films: one-step electrodeposition that provides all constituents from the same electrolyte in a single step and multi-step electro-

deposition that deposits sequentially each constituent from different electrolytes. However, in one-step deposition, it is difficult to obtain the CIGS film with the optimal stoichiometry which is considered as Cu(In_{0.70}Ga_{0.30})Se₂ because of the large difference in the values of equilibrium reduction potential for each constituent. One of the most effective methods to overcome this obstacle is to add a complexing agent into the solution bath because the complexing agent may bring closer the individual reduction potentials. Beside that, complexing agents may alter the deposition mechanism of the film to facilitate the desired or to inhibit the undesired deposition process. However, in acidic bath which is usually used in electrodeposition of CIGS, the complexing abilities of the complexing agents on metal ions are diminished by H⁺. The effect of different acids on the electrodeposition is different. In previous work we have found that sulfamic acid seems to be the good choice [6]. Some other groups have also used the combination of potassium biphthalate (KHP) and sulfamic acid as the complexing agent [7,8]. In this work, by varying sulfamic acid concentration, we studied the role of this acid in improvement of quality of CIGS films, mainly in obtaining the optimal stoichiometry.

Experiments

The cyclic voltammetry studies and the potentiostatically electrodeposition process were carried out using a potentiostat/galvanostat model Autolab 3020 N in a

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three-electrode configuration where the reference electrode was Ag/AgCl, the counter electrode was a Pt spiral wire and the working electrode was a Mo/soda-lime glass substrate. The base electrolyte contained 120 ml deionized water, 350 mM LiCl as supporting agent. Complexing agent was a mixture of 25 mM KHP (Potassium Hydrogen Phthalate) and H₃SNO₃ (sulphamic acids) with the concentration ranging from 0 mM to 40 mM. The pH of the solution varied from 3.09 to 2.26 as concentration of sulfamic acid changed from 0 mM to 40 mM. The concentrations of CuCl₂, InCl₃, Ga(NO₃)₃, and H₂SeO₃ were 20 mM, 30 mM, 40 mM and 20 mM, respectively. The cyclic voltammetry was carried out in the range of potentials from -1.2 V to 0.0 V vs. Ag/AgCl at the scan rate of 20 mV/s. The first scan was in negative direction. The electrodepositions (ED) were processed at the potentials of -0.9 V for 20 minutes. The annealing process was carried out in Ar at 550 °C for 60 minutes. The concentration of the films grown by ED was determined by EDS, the morphology was examined by SEM and the crystallinity was examined by XRD.

Results and Discussion

Effect of sulfamic acid on electrodeposition of Cu(InGa)Se₂ - Cyclic voltammetry results

Voltammogram of unitary Cu, Ga, In, and Se in solutions with different concentration of sulfamic acid.

Fig. 1 presents the voltammograms of the CuCl₂ solutions with different concentration of sulfamic acid. We can see that all voltammograms have three peaks, one at about 0.15 V, one at about -0.4 V and one at about -0.9 V vs. Ag/AgCl. We suggest that the peak at 0.15 V relates to the process:



The peak at -0.4 V can be assigned to the process:

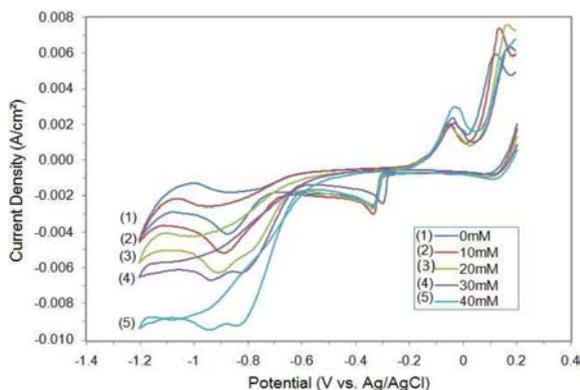
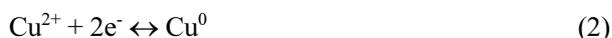


Fig. 1. Voltammograms of the CuCl₂ solutions with different concentration of sulfamic acid.

It means that the previously formed CuCl₂⁻ is an intermediate in the cupric complex reduction to metallic copper. The peak at -0.9 V may correspond to the H⁺ reduction into H₂. As seen in the figures, there is not significant change in the position as well as in the height of the first and second peaks after adding sulfamic acid, except a positive shift of the second peak when the sulfamic acid concentration is 30 mM. In other words, sulfamic acid does not affect on the reduction of Cu ions. In contrast to that, the degree of H⁺ reduction into H₂ decreases as the sulfamic acid concentration increases. This variation is due to the fact that sulfamic acid has a larger molecule volume than H₂O so that the concentration of H⁺ in the electric double layer will decrease with adding sulfamic acid.

Fig. 2 shows the change in the voltammograms for InCl₃ solutions containing different concentration of sulfamic acid. In this figure, the reduction peak of In³⁺ to In at -0.95 V starts appearing after adding 10 mM sulfamic, becomes strongest when the solution contains 20 mM sulfamic acid. Further increasing the concentration of sulfamic acid causes a decrease of In³⁺ reduction. The increase of In³⁺ reduction with sulfamic concentration at the low concentration range can be attributed to the complexation of sulfamic and In³⁺. The decrease of In³⁺ reduction at the high sulfamic acid concentration is due to the decrease of In³⁺ ion concentration in the electric double layer.

Fig. 3 is the CV results which show the effect of sulfamic acid on the reduction of Ga³⁺. In these voltammograms, the peaks at -0.9 V can be assigned to the reduction of Ga³⁺ to Ga and the peaks at -1.05 V should be assigned to the H⁺ reduction into H₂. We can see clearly that the height of the Ga reduction peaks increases while the height of H⁺ reduction into H₂ peaks decreases with increasing the concentration of sulfamic acid. It means that sulfamic acid facilitates the first reduction process but inhibits the later one.

The voltammogram for H₂SeO₃ presented in Fig. 4 shows the effect of sulfamic acid on reduction of H₂SeO₃ to Se. For the cases of solutions containing more than 10 mM sulfamic acid, we can see two strong

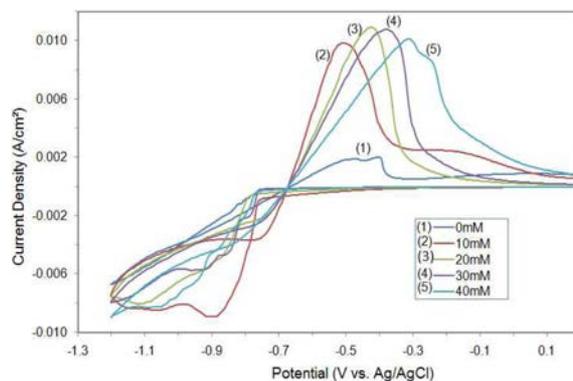


Fig. 2. Voltammograms of the InCl₃ solutions with different concentration of sulfamic acid.

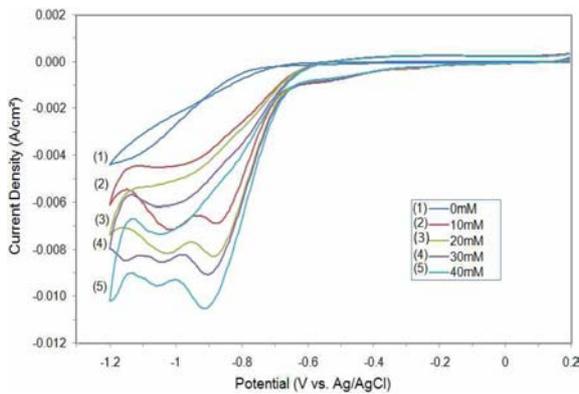


Fig. 3. Voltammograms of the $\text{Ga}(\text{NO}_3)_3$ solutions with different concentration of sulfamic acid.

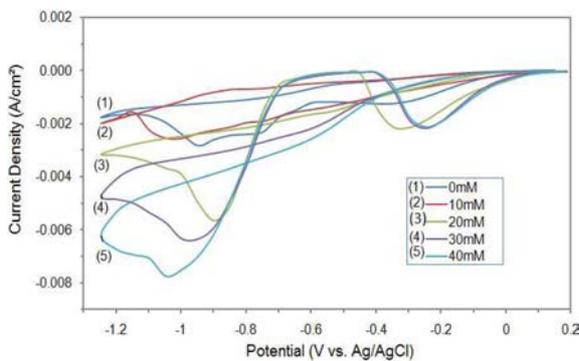
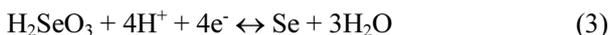
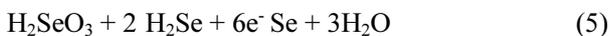
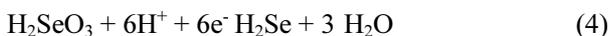


Fig. 4. Voltammograms of the H_2SeO_3 solutions with different concentration of sulfamic acid.

peaks, one at -0.3 V and one at -1.0 V vs. Ag/AgCl. The first peak is likely related to the reduction of H_2SeO_3 directly to Se, following the equation:



We suggest the second peak corresponding to the complex process described by the equations:



This suggestion is similar to those reported by S. Massacesi et al. [9] and K. K. Mishra et al. [10]. The increase of the height of both peaks with increasing sulfamic concentration indicates that adding sulfamic acid has promoted both processes. The increase of the second peak also support our suggestion about the nature of this peak because the H^+ reduction into H_2 is expected to decline after adding sulfamic acid.

Voltammogram of binary Cu-Se system

Fig. 5 illustrates the voltammograms for solutions containing 20 mM CuCl_2 , 20 mM H_2SeO_3 and different concentration of sulfamic acid. There are some differences between these voltammograms and those of unitary Cu

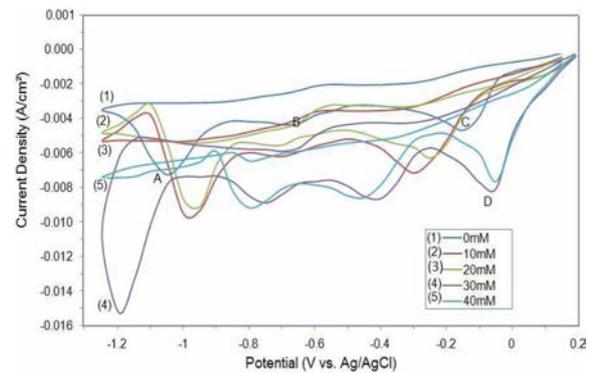


Fig. 5. Voltammograms of solutions containing CuCl_2 , H_2SeO_3 and different concentration of sulfamic acid.

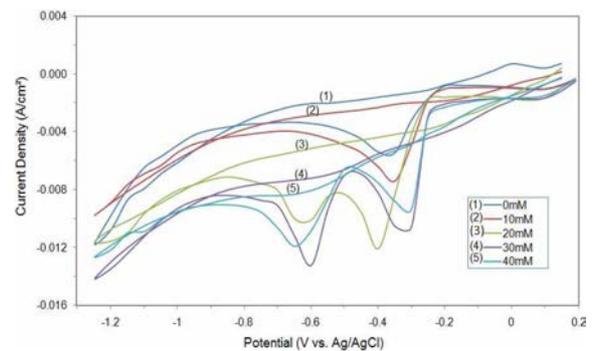


Fig. 6. Voltammograms of the quaternary Cu-In-Ga-Se solutions with different concentration of sulfamic acid.

and Se systems. For the solutions with low sulfamic concentration, we can see three peaks. The peak at about -1.0 V (named peak A) is again assigned to the reduction processes of H_2SeO_3 which have been described in the preceding section. The first notable difference is the appearance of the peak at -0.7 V (named peak B). This peak may still relate to the processes described by Eq. 4 and Eq. 5, that is, these processes occur at a more positive potential due to an induced reaction.

Another notable difference is the position of the peak at about -0.2 V (named peak C) which should relate to the reduction of Cu^{2+} and/or Se^{4+} described by Eq. 2 and/or Eq. 3. Comparing to their equilibrium potential where Cu^{2+} or Se^{4+} alone is reduced, we can see that this peak has a positive shift. The origin of this phenomenon can be attributed to the formation of a Cu-Se phases. The formation of Cu-Se phases is considered as an undesired process because Cu-Se phases are highly conductive, cause shunt paths and therefore diminish the performance of CIGS solar cell. The CV feature described above is remained in the solutions with concentration of sulfamic acid from 0 mM to 20 mM. A strong influence of sulfamic acid on deposition of Cu-Se system has been observed in the solutions containing 30 mM and 40 mM sulfamic acid. Notable evidences of this influence include: (i) the appearance of a peak at about -0.07 V (named peak D) which may be due to the reduction of Cu^{2+} to Cu^+ according to

Table 1. EDS composition of the as-deposition CIGS samples grown at -0.9 V from solutions with different concentration of sulfamic acid.

Concentration of sulphamic acid (mM)	Atom (%)				Stoichiometry
	Cu	In	Ga	Se	
0	24.7	10.5	3.7	61.1	CuIn _{0.42} Ga _{0.15} Se _{2.47}
10	23.5	15.2	6.2	55.1	CuIn _{0.64} Ga _{0.26} Se _{2.34}
20	23.4	15.5	6.7	54.4	CuIn _{0.66} Ga _{0.29} Se _{2.32}
30	23.3	16.1	7.5	53.1	CuIn _{0.69} Ga _{0.32} Se _{2.28}
40	23.8	15.6	8.3	52.3	CuIn _{0.65} Ga _{0.34} Se _{2.19}

Table 2. EDS composition of the post-annealing CIGS samples grown at -0.9 V from solutions with different concentration of sulfamic acid.

Concentration of sulphamic acid (mM)	Atom (%)				Stoichiometry
	Cu	In	Ga	Se	
0	26.5	12.2	5.1	56.2	CuIn _{0.46} Ga _{0.19} Se _{2.13}
10	24.9	16.1	7.5	51.5	CuIn _{0.65} Ga _{0.30} Se _{2.07}
20	24.4	16.5	7.8	51.3	CuIn _{0.67} Ga _{0.32} Se _{2.10}
30	25.0	17.2	8.2	49.6	CuIn _{0.69} Ga _{0.32} Se _{1.98}
40	25.1	16.4	8.7	49.8	CuIn _{0.66} Ga _{0.34} Se _{1.98}

Eq. 1, (ii) the negative shift of the peak C from -0.2 V to -0.4 V and (iii) the vanishing of the peak A. The negative shift of the peak C is an interesting result because it indicates that the formation of Cu-Se phases can be inhibited by using sulfamic acid as the complexing agent.

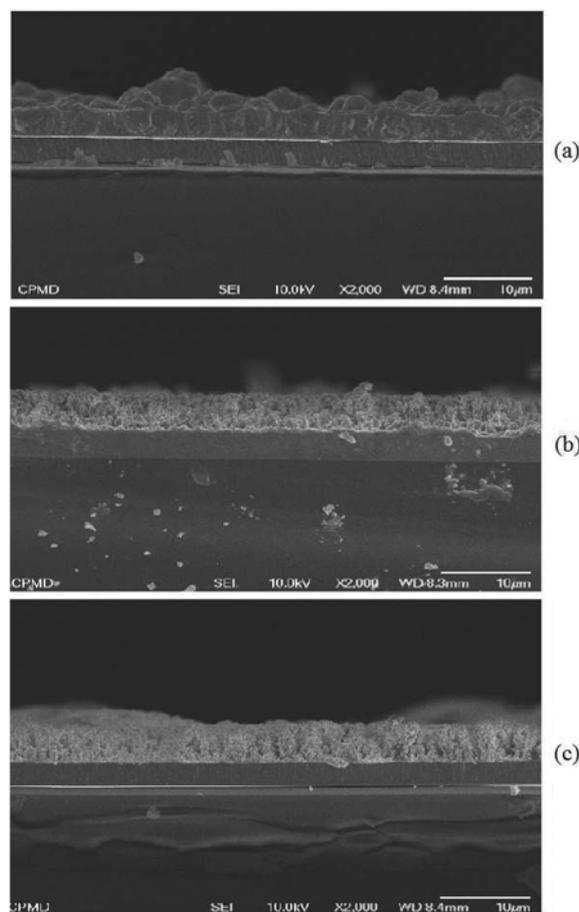
Voltammogram of quaternary Cu-In-Ga-Se

Fig. 6 compares the voltammograms of quaternary Cu-In-Ga-Se for solutions containing sulfamic acid with different concentration. In hole range of sulfamic concentration, we can observe two peaks, one at 0.15 V which relates to the reduction of Cu²⁺ to Cu⁺ and one at about -0.4 V which relates to the reduction of H₂SeO₃ directly to Se, according to Eq. 3. The reduction peaks of In³⁺ and Ga³⁺ are too weak to discern in these voltammograms. A peak at about -0.7 V starts appearing in the voltammogram of the solution with 20 mM sulfamic acid and then increases with increasing sulfamic acid concentration. This peak, as mentioned above, may be assigned to the underpotential deposition process of H₂SeO₃ caused by the formation of Cu-Se phase. It means that highly concentration of sulfamic acid may promote the formation of Cu-Se phases. Therefore, we should take this fact into consideration when choosing the appropriate sulfamic concentration.

Effect of sulfamic acid on composition of CIGS films

Effect of sulfamic acid on composition of as-deposited CIGS films

Table 1 presents the EDS composition of the as-

**Fig. 7.** The cross sectional micrographs of the typical as-deposited samples

deposition CIGS films grown at -0.9 V from solutions with different concentration of sulfamic acid. The first remarkable note is that the concentration of In and Ga is very low in the absent of sulfamic acid and then increases abruptly after adding 10 mM this agent. We also can see that the Ga content increases much faster than the In content as the sulfamic concentration increases continuously. Consequently, the Ga/In ratio increases with increasing sulfamic acid concentration. This observed result brings about the way to tune this ratio to achieve the desired composition. The level of deposited Cu is stabilized at about 23-24 at. % with changing sulfamic concentration. This observation can be expected from CV results which show that sulfamic acid is not conducive to reduction of Cu ions. The combination of the invariance of Cu level and the increment of In and Ga contents leads to a gradually decrease of Se content.

Effect of sulfamic acid on composition of post-annealing CIGS films

Table 2 presents the EDS composition of the post-annealing CIGS films. The notable difference between compositions of the post-annealing and the as-deposited films is the decrement of Se content which is

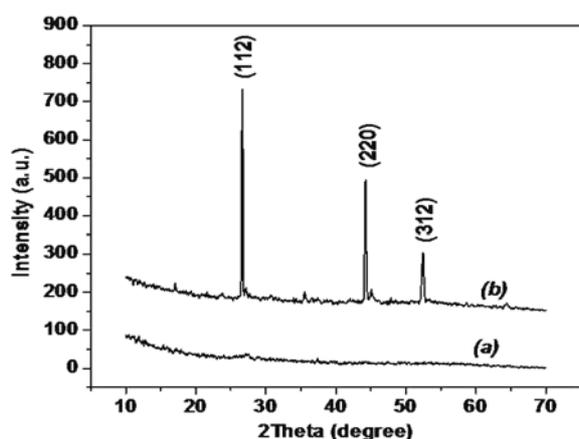


Fig. 8. Typical XRD patterns for as-deposited samples and for post-annealing samples.

due to the high volatile rate of Se during annealing process. As a consequence, the levels of Cu, In, and Ga increase slightly. It is interesting to note that the composition of the films has reached to an almost stoichiometry of chalcopyrite compound after annealing.

Effect of sulfamic acid on thickness, morphology and crystallinity

Fig. 7 is the cross sectional micrograph of the typical as-deposited samples, namely the ones grown from solutions with (a) 0 mM, (b) 20 mM and (c) 40 mM sulfamic acid. Comparing these micrographs, we can see that the higher concentration of sulfamic acid is added into the solution, the thicker films can be produced. This observation reveals that the presence of sulfamic acid has promoted the deposition of CIGS film. Apparently, all films have poor crystallinity with the porous, ununiform and polyphasic structure. However, these micrographs also indicate that sulfamic acid can develop the surface morphology. This role of sulfamic acid can be explained by the ability of this agent to lessen the H^+ reduction into H_2 which can damage the surface of the films.

In all cases of as-deposited samples, the XRD patterns exhibit a nanocrystalline and/or amorphous structure. Y. Lai et al. [11] has observed a similar XRD result and attributed this feature to the high electrode reaction rate and excessive concentration polarization at the potential in the range -0.77 to -0.95 V. The XRD patterns of the post-annealing samples are almost identical with the typical peaks of the CIGS chalcopyrite structure,

namely (112), (220) and (312). For that reason, we only show in Fig. 8 one typical XRD pattern for as-deposited samples (a) and one typical XRD pattern for post-annealing samples (b).

Conclusions

Sulfamic acid has been found to be a suitable complexing agent. It can promote the electrodeposition of CIGS film, especially it can increase the Ga content. Beside that, with an appropriate concentration, sulfamic acid can inhibit the underpotential deposition of Cu-Se phases and the H^+ reduction into H_2 which are considered as the undesired process. The desired $Cu(In_{0.70}Ga_{0.30})Se_2$ stoichiometry has been obtained in the films grown from solution which contains 20-30 mM sulfamic acid. Fabrication of solar cell devices using the obtained CIGS films are in progress.

Acknowledgements

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