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Study of the Effect of Sulfamic Acid on Formation Cu-Se Compounds by CV and EQCM

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Abstract: A combination of Cyclic Voltammetry (CV) and Electrochemical Quartz Crystal Microbalance (EQCM) has been used to study the effect of sulfamic acid as a complexing agent on the formation of Cu-Se compounds. It has been found that sulfamic acid does not affect the deposition of Cu in the absent of Se. However, when Cu and Se are simultaneously, sulfamic acid was found to affect strongly the formation of Cu-Se compounds, namely it causes and facilitates the reactions forming Cu-Se compounds. Furthermore, at high concentration, sulfamic acid causes a mass-loss process, leading to a change of composition and a poor surface morphology. A suitable concentration of sulfamic acid can be concerned from these studies.

Keywords: Cyclic voltammetry, EQCM, Cu-Se compounds, electrodeposition, thin films.

1. Introduction

One-step electrodeposition of $Cu(In_{1-x}Ga_x)Se_2$ (CIGS) has become the focus of many research groups in the field of solar energy because it is economic, simple, and allows to deposit over large surface areas. However, in one-step deposition, it is difficult to obtain the CIGS film with the optimal stoichiometry because of the large difference in the values of equilibrium reduction potential for each constituent. Adding a complexing agent into the solution bath is one of useful methods to overcome this difficulty because complexing agent may alter the deposition mechanism of the film to facilitate the desired or to inhibit the undesired deposition process. Some researchers have found that sulfamic acid can be used as a suitable complexing in electrodeposition of CIGS layer [1- 3]. In our previous studies on the role of acid sulfamic in deposition of CIGS carried out by Cyclic Voltammetry technique [4], we have observed the significant changes of the Voltammograms after introducing sulfamic acid with different concentration, especially in case of Cu-Se binary system. Based on CV

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analysis, we have also proposed some explanations for these observations. However, due to the fact that the CV technique only provides the deposition current during potential scanning, our explanation may be less convincing. Because the formation of CIGS is generally agreed to undergo via the formation of Cu-Se phases, the deposition of Cu-Se system is the most interested [5]. In the present paper, we reported our works on the effect of sulfamic acid on the electrodeposition of Cu-Se compounds by using the Electrochemical Quartz Crystal Microbalance (EQCM) which measures the effective deposited mass simultaneously with the deposition current. By application of Faraday's law, this combination can provide more clearly information about deposition mechanism of CIGS layer. According to our knowledge, only a few EQCM studies on the Cu-Se system have been reported so far [6, 7]. However, as mentioned above, our study focuses on the effect of sulfamic acid.

2. Experiments

A combination system including an Autolab PGSTAT30 potentiostat/galvanostat and a KSV QCM-Z500 treat (Hanoi University of Science, Vietnam) were used for cyclic voltammetry and microgravimetry studies. The QCM-Z500 was used as an EQCM when it was equipped with an electrochemical chamber.

The sensors used in our experiments are the AT-cut 5 MHz gold coated quartz crystals (QSX 301 – standard gold, Q-sense) which has 14 mm diameter of the quartz crystal and 0.785 cm^2 projected area of the Au electrode.

The potentiostat connects to the EQCM via a three-electrode configuration where the working electrode is one side of the quartz crystal (the Au film), the reference electrode is Ag/AgCl 3M KCl electrode and the counter electrode is one of the Pt electrode poles. All the cyclic voltammograms and microgravimetry scans were measured at a speed of 10 mV/s and they were scanned first to the negative direction.

Each measurement used 2 ml electrolyte which contained deionized water, 350 mM LiCl as supporting agent, 25 mM KHP (Potassium Hydrogen Phthalate) and H_3SNO_3 (sulphamic acids) with the concentration ranging from 0 to 40 mM as the complexing agents. The electrolyte for study of Cu deposition was added 20 mM $CuCl_2$ and then, for study of Cu-Se system, this electrolyte was added 20 mM H_2SeO_3. Before measurements, the electrolytes were dissolved by ultrasonic for 5 minutes.

The electrodepositions (ED) were processed at the potentials of -0.3, - 0.6 and - 0.9 V for 20 minutes. The concentration of the films grown by ED was determined by Energy Dispersive Spectroscopy (EDS) and the micro-structure surface of the films was determined by Atomic Force Microscopy (AFM).

In order to analyze the processes taking place at the electrode surface, the primary EQCM data may be treated by different ways. A simple and straightforward way is to combine the Sauerbrey equation with the Faraday's law.

The Sauerbrey equation describes the correlation between the mass change (Δm) of the quartz crystal surface and the frequency change (Δf) caused by Δm

$$\Delta f = -\frac{2f_0^2}{A(\mu\rho)^{1/2}}\Delta m = -K\Delta m \qquad (1)$$

where f_0 is the fundamental resonant frequency of the crystal in the absence of the deposited mass ($f_0 = 5\,\mathrm{MHz}$), A is the geometric area of electrode, and μ is the shear modulus ($\mu = 2.947\times10^{11}\,\mathrm{gcm^{-1}s^{-2}}$) and ρ is the density of quartz ($\rho = 2.648\,\mathrm{gcm^{-3}}$). All the constants in the equation can be included into a single constant (K) which can be determined experimentally by electrodepositing Cu from $CuCl_2$ bath under potentiostatic conditions (-0.4 V) for 3 minutes, considering that the Cu electrodeposition process is 100% efficient. A K value of 71.6 $\mathrm{Hz}/\mu\mathrm{g}$ was obtained, which is very close to the theoretical value computed from the Sauerbrey equation (72.1 $Hz/\mu g$). For this reason, Eq. 1 is used for the further calculations of the mass, with a proportionality factor equal to 71.6 $\mathrm{Hz}/\mu\mathrm{g}$.

The charge consumed (ΔQ) that is related to the mass change of the deposit according to Faraday's law:

$$\Delta Q = \frac{Fz}{M}\Delta m \qquad (2)$$

where F is the Faraday constant (96485.31 $\mathrm{C/mol}$), z - the number of electrons consumed in the reaction, Δm - the mass change of the deposit during the reaction, and M - the molar mass of the corresponding chemical species.

By defining the signs of z, Δm, and M appropriately [7, 8], one obtains

$$\Delta f = \frac{K\Delta QM}{Fz} = \frac{K}{F}\frac{M}{z}\Delta Q \qquad (3)$$

In order to obtain the M/z values, the frequency change (Δf) is plotted as a function of the charge consumed (ΔQ). The slope of such a plot ($d\Delta f/d\Delta Q$) is obtained as a derivative of Eq. (3)

$$M_e = \frac{M}{z} = \frac{d\Delta f}{d\Delta Q}\frac{F}{K} \qquad (4)$$

The theoretical M/z is simply the change of the molar mass of the deposit divided by the number of electrons involved in the reaction. The experimental M/z values obtained by this way do not involve any hypothesis about the reaction mechanisms but still represent directly the primary data. On the other hand, a theoretical M/z value is easily calculated for any suggested reaction. An agreement between the observed and theoretical M/z values gives thus a quite solid proof for the dominance of the suggested reaction while differences call attention for other mechanisms.

3. Results and discussions

3.1. Deposition mechanism of copper- CV-EQCM combination studies

The operation of CV-EQCM combination system was firstly checked by measuring the CV of the base solution which contains only water, LiCl, KHP and H_3SNO_3. We can see in Fig.1 that, within the scan range, there is not any reduction peak. It means that there is not any reduction process taking place in this solution. At high negative potential the current decreases rapidly when hydrogen reduction starts taking place. Fig. 2 presents the voltammograms of 20 mM $CuCl_2$ in the solutions with different sulfamic concentration. All voltammograms show similar behavior with two peaks, one at about 0.08 V and one at about -0.3 V vs. Ag/AgCl. We suggest that the peak at 0.08 V relates to the process:

$$Cu^{2+} + 2Cl^- + e^- \leftrightarrow CuCl_2^- \quad (5)$$

The peak at -0.3 V can be assigned to the process:

$$CuCl_2^- + e^- \leftrightarrow Cu^0 + 2Cl^- \quad (6)$$

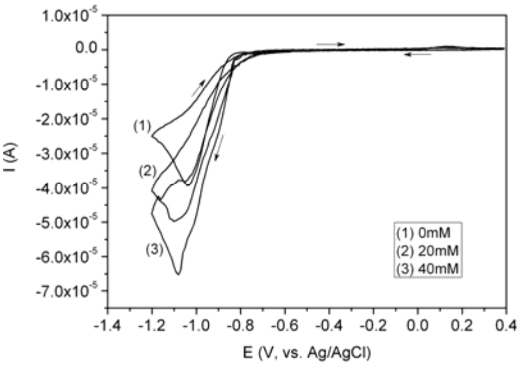

Fig. 1. Voltammograms of the base solutions with different concentration of sulfamic acid.

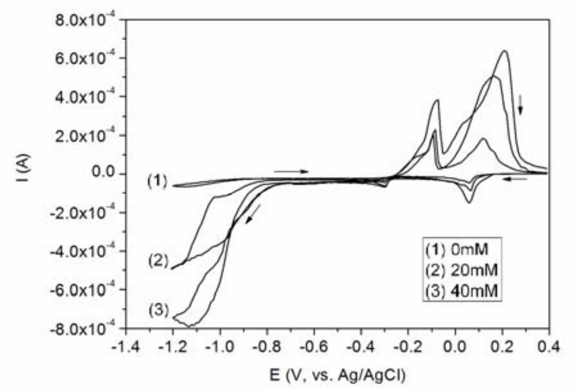

Fig. 2. Voltammograms of the $CuCl_2$ solutions with different concentration of sulfamic acid.

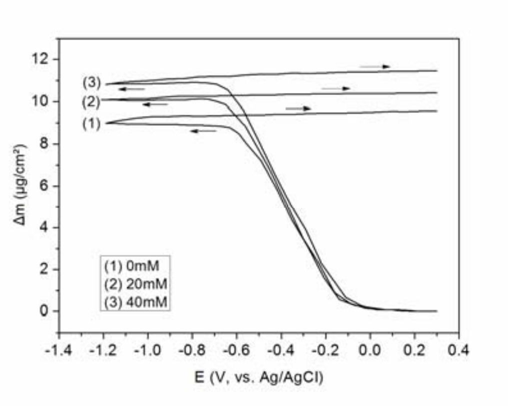

Fig. 3. The mass change at the gold EQCM in $CuCl_2$ solutions with different concentration of sulfamic acid.

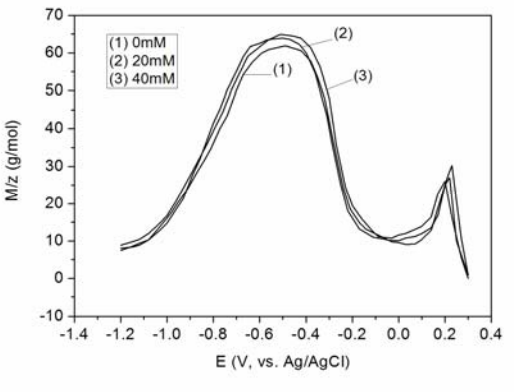

Fig. 4. The equivalent atomic mass (M/z) obtained at the gold EQCM in $CuCl_2$ solutions with different concentration of sulfamic acid.

Our suggestion is in agreement with those proposed by L. M. Abrantes et al [9]. This suggestion is confirmed by the data of EQCM which are shown in Fig. 3 and Fig. 4. In Fig. 3, the mass gain curve associated with deposition of Cu starts increasing at the potential of about -0.1 V instead of 0.08 V. In addition, we can see the rate of deposition increasing slightly with adding sulfamic concentration. Fig.4 presents the M_e vs. potential plots. At the beginning of the scan, the plots have an unexpectation peak which may be due to a sudden change in interfacial potential. After that, the plots increase and at the potential of 0.7 V they reach to the value of about 63 g/mol which is very close to the theoretical value of 63.55 g/mol corresponding to the process described by Eq. (6).

3.2. Deposition mechanism of Cu-Se compounds- CV-EQCM combination studies

Fig. 5 shows the voltammograms and Fig. 6 shows simultaneously the mass changes at the gold EQCM in solutions containing $CuCl_2$, H_2SeO_3 and sulfamic acid with different concentration. We can see that when both $CuCl_2$ and H_2SeO_3 present simultaneously, the current-voltage curves change significantly compared to those of Cu unity system, especially in case of high concentration of sulfamic. In curve 1, two peaks corresponding to reduction of copper have become two waves while a new peak has appeared at -0.42 V which should relate to the direct reduction of Se according to the equation:

$$H_2SeO_3 + 4H^+ + 4e^- \leftrightarrow Se\ (s) + 3H_2O \qquad (7)$$

M/z = 19.74 g/mol

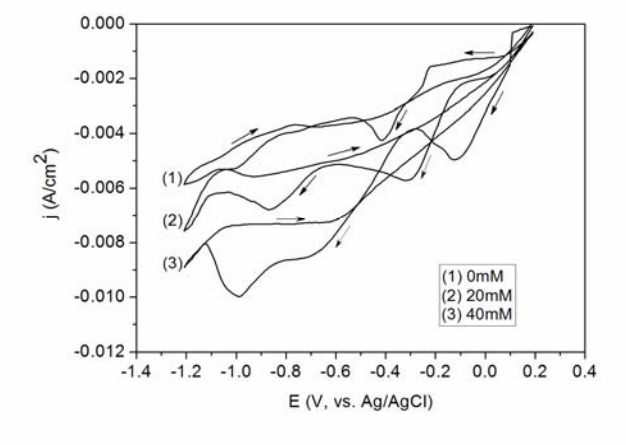

Fig. 5. Voltammograms of solutions containing $CuCl_2$, H_2SeO_3 and sulfamic acid with different concentration.

When sulfamic acid is added into solution (curve 2), it is clear that the reduction current increases and shifts to positive potential. In previous work, we have also observed the positive shift of reduction current in Se unity system by adding sulfamic acid [4]. Furthermore, a new strong peak can be observed at -0.85 V in curve 2. An overlap between Se direct reduction and copper reduction due to the strong positive shift of the former process has been also observed. Further adding sulfamic acid, the reduction current (curve 3) continuously moves to positive potential direction. Besides that, a strong peak at -0.95 V appears. In our previous work on Mo substrate [4], we have observed similar effect of sulfamic acid on the behaviors of voltammogram and have proposed some explanations. However, as mentioned above, due to the limitation of information provided by CV technique, our explanations may be less convincing.

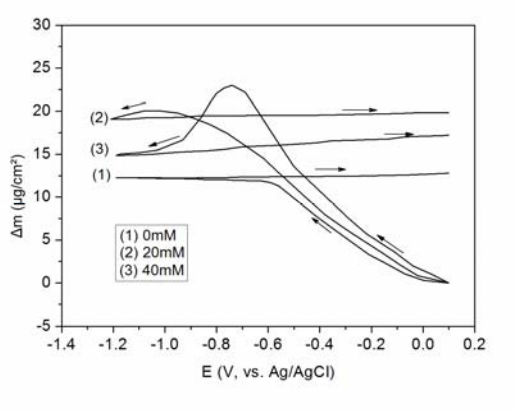

Fig. 6. The mass change at the gold EQCM in solutions containing $CuCl_2$, H_2SeO_3 and sulfamic acid with different concentration.

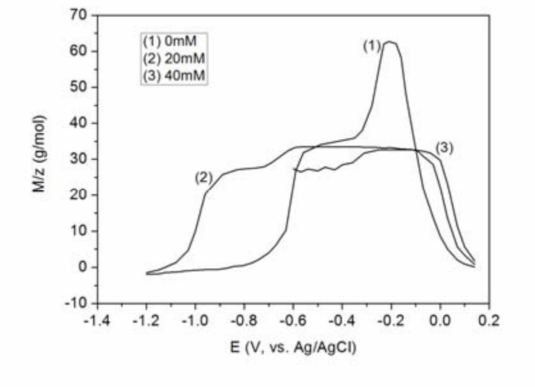

Fig.7. The equivalent atomic mass (M/z) obtained at the gold EQCM in solutions containing $CuCl_2$, H_2SeO_3 and sulfamic acid with different concentration.

In order to elucidate the reduction processes corresponding to these observations, we use the data of EQCM technique. As seen in Fig. 6, the mass deposited on gold sensor during potential scan starts increasing from the beginning of the scan. In case of the solution without sulfamic acid, the deposition finishes at the potential of - 0.6 V. When sulfamic acid is present, the deposition becomes stronger and finishes at more negative potential. It is worth to note that, when higher concentration of sulfamic acid is introduced into the electrolyte, the Δ*m* plot reaches to a maximum and then decreases, indicating that a mass loss process has occurred.

The deposition mechanism can be verified more clearly by using the equivalent atomic mass data (M_e) which is shown in Fig. 7. In the absence of sulfamic acid, at the potential of - 0.2 V, the M_e value is close to 63 g/mol, corresponding to the redox process of copper described by Eq. (6). As the Se reduction begins, the value of M_e reduces to value of about 35 g/mol and then decreases slightly until the potential of - 0.6 V. At - 0.6 V the M_e plot decreases abruptly to zero, indicating that at the potential more negative than -0.6 V, no deposit is formed. This feature of M_e is in agreement with the plot 1 in Fig.6. Concerning the value of M_e at the potential range from - 0.3 V to - 0.6 V, we suggest that this value simply is an intermediate value between 63.55 g/mol of pure copper deposition and 19.74 g/mol for pure Se deposition, depending on the ratio of $CuCl_2^-$ and H_2SeO_3. If we call this ratio as x, the deposit stoichiometry should be $CuSe_x$. When 20 mM sulfamic acid is added into solution, as can be seen in the curve 2, the overlap region of codeposition process widens and becomes a platieu with the value as the same as of curve 1, i.e, about 35 g/mol. This observation can be attributed to the positive shift of Se reduction. At more negative potential, the M_e curve decreases to the value of about 24 g/mol, remains this value until the potential of -1.0 V and then goes down rapidly to zero. This value of M_e should result from one of following reactions:

$Cu(NH_2SO_3)^+ + H_2SeO_3 + 4H^+ + 6e^- \leftrightarrow CuSe + 3H_2O$ (8)

M/z = 23.75 g/mol

$2Cu(NH_2SO_3)^+ + H_2SeO_3 + 4H^+ + 8e^- \leftrightarrow Cu_2Se + 3H_2O$ (9)

M/z = 25.75 g/mol

$3Cu(NH_2SO_3)^+ + 2H_2SeO_3 + 8H^+ + 14e^- \leftrightarrow Cu_3Se_2 + 6H_2O$ (10)

M/z = 24.89 g/mol

It means that in the region from -0.7 V to -1.0 V, the formation of Cu-Se compounds has occured. As increasing the concentration of sulfamic acid, we can observe again in curve 3 an overlap region corresponding to a codeposition process of copper and selenium and a region where the formation of Cu-Se compounds takes place. By comparing the curve 3 to the curve 2, we can see two significant differences. First, the process forming Cu-Se compounds occures earlier in curve 3 than in curve 2. Second, the curve 3 terminates at the voltage of -0.8 V because from this voltage it is impposible to determine value of M_e. The second phenomena should relate to a mass-loss process that has been mentioned above. Marlot et al. has observed a mass loss process when they studied the deposition of Cu-Se by using a Rotating EQCM [6]. They have attributed this process to the reduction of $CuSe_x$ formed previously into CuSe, Cu_3Se_2 and/or Cu_2Se compounds. We agree to their explaination but in our case, we express that the mass-loss phenomena is a result from a reduction of a rich Se compound to a less rich Se compound, for example:

$2CuSe + 2H^+ + 2e \leftrightarrow Cu_2Se + H_2Se$ (11)

In solution with high concentration of sulfamic acid, the formation of Cu-Se takes place earlier and stronger, leading to a mass-loss process.

3.3. Composition and surface morphology studies

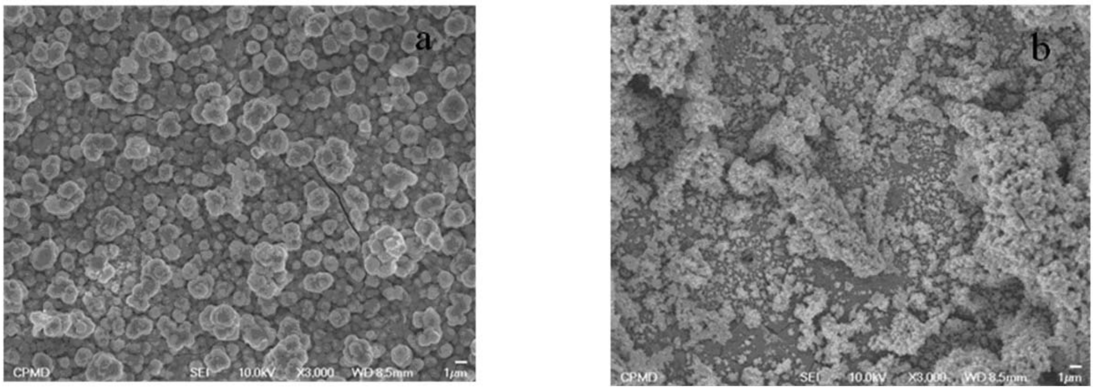

Fig. 8a-b. AFM images of two samples deposited from solutions containing 20 mM and 40 mM sulfamic acid at potential of -0.9 V.

Fig. 8a-b show AFM images of two samples deposited from solutions containing 20 mM and 40 mM sulfamic acid at potential of -0.9 V. We chose this deposition potential because according to the above results, at this potential, the deposition mechanism of these two samples were expected to be different. Moreover, this potential is also the potential that we have chosen to deposite Cu(InGa)Se_2 films because deposition of Ga generally requires a very negative potential. As can be seen, Fig. 8a shows a homogeneous and dense surface which should be the result from the formation of Cu-Se compounds. In contrast with Fig. 8a, Fig. 8b exhibits a poor surface morphology with a porous, ununiform structure. This observation is an evidence of the mass-loss process mentioned in Section 3.2. According to the Eq. 11, during the mass-loss process, the surface of sample releases Se in H_2Se form, bringing about a porous structure. Another evidence of the mass-loss process is the different in composition of these two samples. The composition determined by EDS technique indicates that the sample deposited from solution containing 20 mM sulfamic acid has higher Se concentration than those of the sample deposited from solution containing 40 mM sulfamic acid.

4. Conclusion

The use of a CV-EQCM system is powerful method to study the deposition mechanism of Cu-Se system. The results of this work have explained and confirmed our previous observations and suggestions. Sulfamic acid was found to affect strongly the formation of Cu-Se compounds, namely it causes and facilitates the reactions forming Cu-Se compounds. Furthermore, at high concentration, sulfamic acid causes a mass-loss process, leading to a change of composition and a poor surface morphology. From these studies, a suitable concentration of sulfamic acid should be concerned.

Acknowledgments

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