

EQCM studies of the effect of sulfamic acid on the formation Cu-Se compounds

Dang Thi Bich Hop^a, Pham Hong Quang^b, Duc H. Tran^{c,*}, Do Thi Kim Anh^c, Do Phuc Quan^c Ngo Dinh Sang^d and W.B.K.Putri^e

^aInstitute of Geophysics, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam

^bPetroVietnam University, 173 Trung Kinh, Cau Giay, Hanoi, Vietnam

^cHanoi University of Science, 334 Nguyen Trai, Thanh Xuan, Hanoi, Vietnam

^dNational University of Civil Engineering, 55 Giai Phong, Hai Ba Trung, Hanoi, Vietnam

^eChungbuk National University, Cheongju, 361-763 Korea

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. The values of the equivalent atomic mass (M/z) grown at the gold EQCM sensor during electrodeposition at varying potentials and constant potentials were analyzed to understand the mechanism of the growing process. It was found that sulfamic acid does not affect so much the deposition of Cu in the absence of Se. However, when Cu and Se are present simultaneously, sulfamic acid causes and facilitates the formation of Cu-Se compounds. Furthermore, at a high concentration, sulfamic acid causes a mass-loss process, leading to a change of composition. A suitable concentration of sulfamic acid can be concerned from these studies.

Key word: Cyclic voltammetry, EQCM, Cu-Se compounds, Electrodeposition, Thin films.

Introduction

One-step electrodeposition of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ (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. Some researchers have found that sulfamic acid can be used as a suitable complexing agent in electrodeposition of CIGS layer [1, 2, 3]. In our previous studies on the role of acid sulfamic in deposition of CIGS carried out by Cyclic Voltammetry technique [4], we 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 analysis, we also proposed some explanations for those 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 report 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. 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.

Experimental

A combination system including an Autolab PGSTAT30 potentiostat/galvanostat and a KSV QCM-Z500 treat 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 have 14 mm diameter of the quartz crystal and 0.785 cm² 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.

*Corresponding author:
Tel : +84-989384699
Fax: +84-437823208
E-mail: dhtran@hus.edu.vn

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. The concentration of the films grown by ED was determined by using the energy dispersive spectroscopy (EDS).

Each measurement used 2 ml electrolyte which contained deionized water, 350 mM LiCl, 25 mM KHP (Potassium Hydrogen Phthalate) and H₃SNO₃ (sulfamic acids) with the concentration ranging from 0 mM to 40 mM. The above electrolyte was added 20 mM CuCl₂ for study of Cu deposition and then, was added 20 mM H₂SeO₃ for study of Cu-Se system. Before measuring, the electrolytes were dissolved by ultrasonic for 5 minutes. In potentiostatic deposition (ED), the samples were grown at the potentials of -0.3 V, -0.6 V and -0.9 V for 20 minutes.

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

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

where f_0 is the fundamental resonant frequency of the crystal in the absence of the deposited mass ($f_0 = 5$ MHz), A is the geometric area of electrode, μ is the shear modulus ($\mu = 2.947 \times 10^{11}$ gcm⁻¹s⁻²) and ρ is the density of quartz ($\rho = 2.648$ 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 CuCl₂ bath under potentiostatic conditions (-0.4 V) for 3 minutes, considering that the Cu electrodeposition process is 100% efficiency. A K value of 71.6 Hz/ μ g was obtained, which is very close to the theoretical value computed from the Sauerbrey equation (72.1 Hz/ μ g). For this reason, Eq. 1 is used for the further calculations of the mass, with a proportionality factor equal to 71.6 Hz/ μ g.

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

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

where F is the Faraday constant (96485.31 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

$$\Delta f = \frac{K\Delta Q M}{Fz} = \frac{KM}{Fz}\Delta Q \quad (3)$$

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)

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

The theoretical M/z value is easily calculated for any suggested reactions. This value 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. A good coincidence between the observed and theoretical M/z values gives thus a quite solid proof for the dominance of the suggested reaction. When they are different, they can be related to other mechanisms

Results and Discussions

Potential scanning process

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

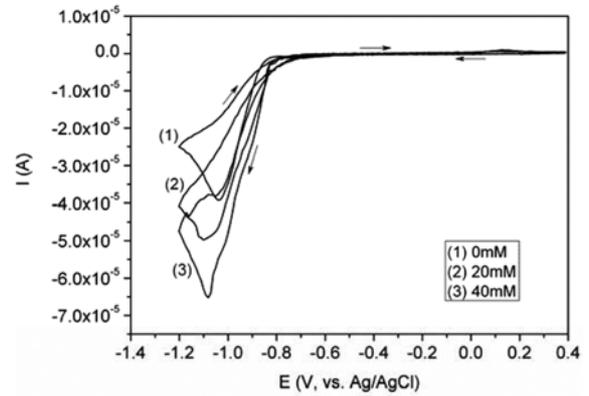


Fig. 1. Voltammograms of the base solutions with different concentration of sulfamic acid.

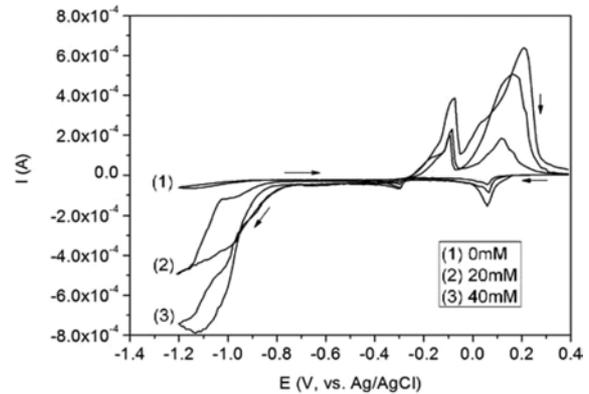
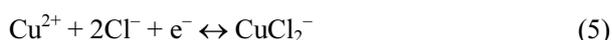
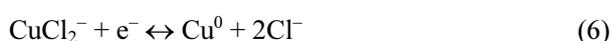


Fig. 2. Voltammograms of the CuCl₂ solutions with different concentration of sulfamic acid.

H_3SNO_3 . We can see in Fig.1 that, within the scan range, there is not any reduction in 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:



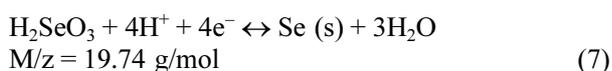
The peak at -0.3 V can be assigned to the process:



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 a un-expectation peak which may be due to a sudden change in interfacial potential. After that, the plots increase and at the potential of -0.5 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).

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 concentrations. We can see that when both CuCl_2 and H_2SeO_3 are 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 the reduction of copper become two waves while a new peak appears at -0.42 V which should relate to the direct reduction of Se according to the equation:



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,

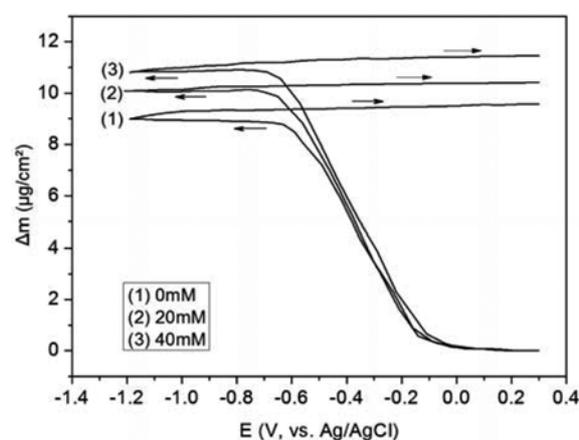


Fig. 3. The mass change at the gold EQCM in CuCl_2 solutions with different concentration of sulfamic acid.

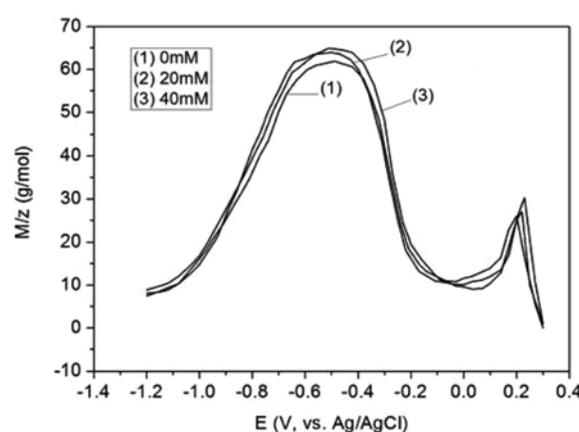


Fig. 4. The equivalent atomic mass (M/z) obtained at the gold EQCM in CuCl_2 solutions with different concentration of sulfamic acid.

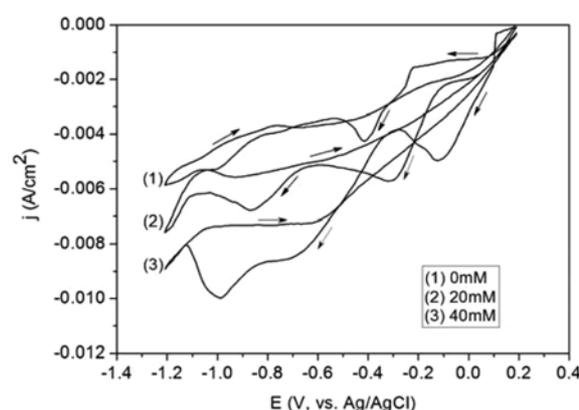


Fig. 5. Voltammograms of solutions containing CuCl_2 , H_2SeO_3 and sulfamic acid with different concentration.

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

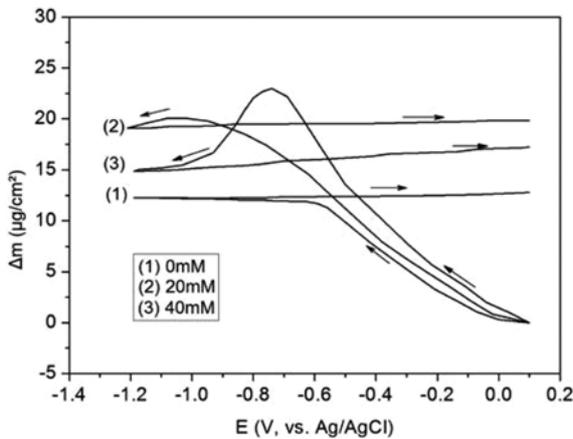


Fig. 6. The mass change at the gold EQCM in solutions containing CuCl_2 , H_2SeO_3 and sulfamic acid with different concentration.

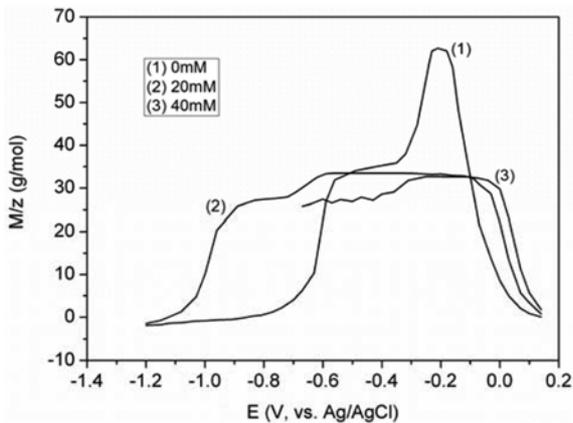


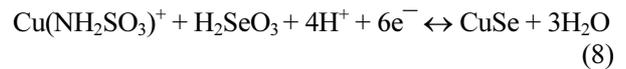
Fig. 7. The equivalent atomic mass (M/z) obtained at the gold EQCM in solutions containing CuCl_2 , H_2SeO_3 and sulfamic acid with different concentration.

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.

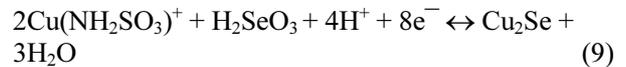
In order to elucidate the reduction processes corresponding to these observations, we use the data of EQCM technique. As seen in Fig. 6, the mass deposited on gold sensor during potential scan starts increasing from the beginning of the scan. In case of the solution without sulfamic acid, the deposition 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 a higher concentration of sulfamic acid is introduced into the electrolyte, the Δm 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

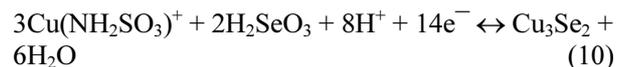
described by Eq. (6). As the Se reduction begins, the value of M_e reduces to value of about 35 g/mol and then decreases slightly until the potential of -0.6 V. At -0.6 V the M_e plot decreases abruptly to zero, indicating that at the potential more negative than -0.6 V, no deposit is formed. This feature 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 plateau 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 the following reactions:



$$M/z = 23.75 \text{ g/mol}$$



$$M/z = 25.75 \text{ g/mol}$$



$$M/z = 24.89 \text{ g/mol}$$

It means that in the region from -0.7 V to -1.0 V, the formation of Cu-Se compounds has been occurred. 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, the two significant differences might be seen. First, the process forming Cu-Se compounds occurs 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 impossible 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

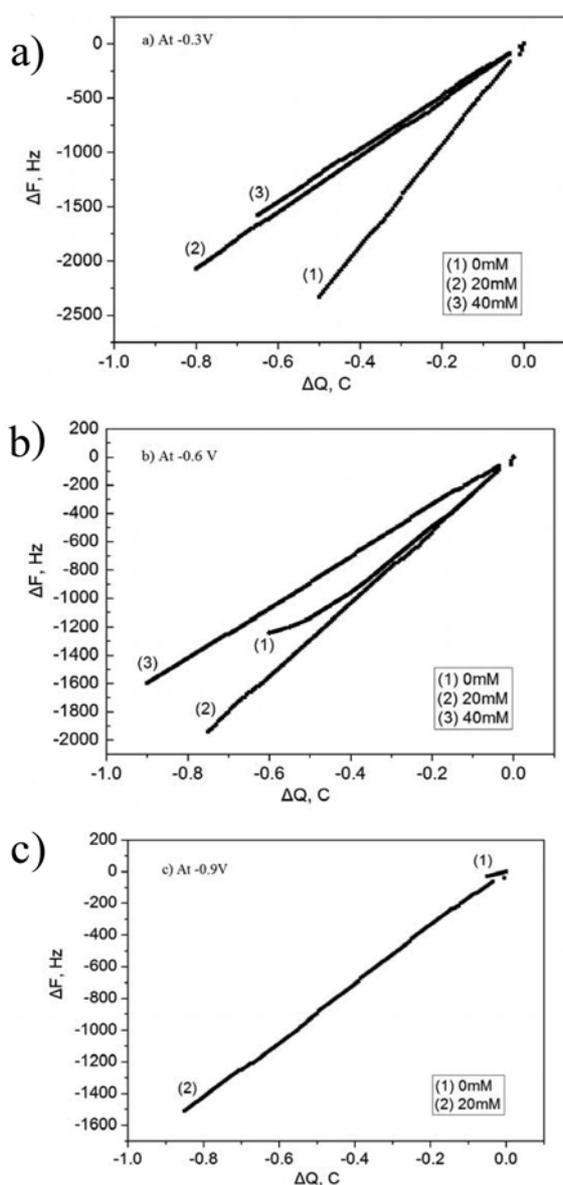


Fig. 8. The Δf vs. ΔQ plots measured in solutions containing different concentration of sulfamic acid at the potentiostatic deposition: a) -0.3 V, b) -0.6 V and c) -0.9 V.

Cu_2Se compounds. We agree to their explanation 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:



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

Potentiostatic deposition

In this study, the Δf vs. ΔQ plots were recorded during the potentiostatic deposition from solutions containing different concentration of sulfamic acid. The

results are illustrated in Fig. 8(a), 8b and 8c corresponding to the potentials of -0.3 V, -0.6 V and -0.9 V, respectively. For the deposition at potential of -0.3 V, as can be seen in Fig. 8(a), the Δf vs. ΔQ plots exhibit the case of a stationary growth, i.e. they are linear over the all deposition time. It is interesting that the the M/z values determined from slope of these plots are almost equal to those deduced from scanning process at the same potentials.

When the depositions take place at -0.6 V, we can see in Fig. 8(b) that the Δf vs. ΔQ profile remains unchanged in cases of the solution containing 20 mM and 40 mM sulfamic acid. Again, these plots give the M/z values which are equal to those deduced from scanning process. In case of solution containing 0 mM sulfamic acid, the Δf vs. ΔQ profile is linear only in the first part of the deposition time and then deviates positively from the ideal variation (dotted line) which corresponds to a stationary deposition with an M/z value of about 30 g/mol. The positive deviation of the Δf vs. ΔQ plot indicates the decrease of M/z value during deposition time. This observation can be understood if we see in Fig. 7 that, at this potential, the curve 1 (for 0 mM sulfamic acid) starts going down rapidly. Thus, the decrease of M/z value is not due to the change in stoichiometry but is mainly due to the decrease of the efficiency of the deposition process.

The Δf vs. ΔQ profiles change dramatically when the depositions take place at more negative potential, namely -0.9 V. At this potential, it is possible to record only the Δf vs. ΔQ profile for the deposition from solution containing 20 mM sulfamic acid with an M/z value of about 24 g/mol. For the solution without sulfamic acid, the plot is very short and is almost horizontal; indicating that there is very little deposit has been formed on the surface of sensor. For the solution containing 40 mM sulfamic acid, the signal of the measurement is extremely noisy so that we cannot record the Δf vs. ΔQ plot. These observations are in agreement with the features shown in Fig 7 at potential of -0.9 V where the M/z values are 0, 24 g/mol and undeterminable for solutions containing 0, 20 and 40 mM sulfamic acid, respectively.

Composition of the samples grown by potentiostatic deposition

As mentioned above, the deposit stoichiometry is written as CuSe_x where x depends on the ratio of Cu atoms to Se atoms co-deposited on the surface of samples. Table 1 lists the x value describing the EDS composition of the samples grown by potentiostatic deposition.

Based on the assumption of the deposition mechanism mentioned in the sessions A and B, we can explain the varying of the composition at different growing conditions.

For the solution not containing sulfamic acid, at the potential of -0.3 V, the deposited layer is Cu rich

Table 1. The x value describing the EDS composition of the samples grown by potentialstatic deposition.

Deposition potential	The concentration of sulfamic acid		
	0 mM	20 mM	40 mM
-0.3 V	0.43	1.8	2.6
-0.6 V	1.6	1.8	5.6
-0.9 V	No deposit	2.2	1.4

compound because in this case, the reduction of Cu dominates. At potential of -0.6 V, the ratio of Cu to Se is 1/1.6, that is only somewhat lower than that expected from the M/z value of 35 g/mol. At -0.9 V it is impossible to get EDS data due to the fact that the layer is so thin.

For the solution containing 20 mM sulfamic acid, at the potentials of -0.3 V and -0.6 V, the Cu-Se stoichiometry is $\text{CuSe}_{1.8}$ which is in accordance with the M/z value of 35 g/mol. It is interesting to note that, at the potential of -0.9 V, where the M/z value is 24 g/mol, the x value should be very high if it is simply based on a co-deposition. Actually, in this case, some reactions have taken place (Eq. 8-10) forming different Cu-Se phases. Considering that the best stoichiometry of CIGS film is $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$, the x value of 2.2 is very noticeable.

For the solution containing 40 mM sulfamic acid, the x values also vary in accordance with M/z values except the case at the potential of -0.9 V. At this condition, a mass loss process may occur relating to the reduction of a rich Se compound to a less rich Se compound.

Conclusions

The use of a CV-EQCM system is a 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 a high concentration, sulfamic acid causes a mass loss process, leading to a change of composition. The concentration of 20 mM of sulfamic acid and the potential of -0.9 V were found to be the most suitable conditions for the deposition of Copper-Selenium layers towards CIGS thin film solar cell application.

Acknowledgments

This work was supported by the NAFOSTED project (103.02.59.09).

References

1. N.D. Sang, P.H. Quang, and L.T. Tu, Communications in Physics 21 [4] (2011) 365.
2. M.E. Calixto, K.D. Dobson, B.E. Mc Candless, R.W. Brikmire, J. Electrochem. Soc. 153 [6] (2006) G521.
3. R.N. Bhattacharya, A.M. Fernandez, Sol. Energy Mater. Sol. Cells. 76 (2003) 331.
4. Pham Hong Quang, Dang Thi Bich Hop, Ngo Dinh Sang, Tran Hai Duc and Le Tuan Tu, Journal of Ceramic Processing Research 13 [2] (2012) s318~s322.
5. S. Menezes, Mater. Res. Soc. Symp. Proc. 426 (1996) 189.
6. A. Marlot and J. Vedel, Journal of The Electrochemical Society 146 [1] (1999) 177-183.
7. M. Kemell, H. Saloniemi, M. Ritala, M. Leskela, Electrochimica Acta 45 (2000) 3737-3748.
8. M. Kemell, H. Saloniemi, M. Ritala and M. Leskela, Journal of The Electrochemical Society 148 [2] (2001) C110-C118.
9. L.M. Abrantes, L.V Araujo. and D. Veli, Minerals Engineering 8 [12] (1995) 1467.