Electrochemical quartz crystal microbalance study of electrodeposition of copper-selenium thin films

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Abstract: The deposition of Copper-Selenium thin films was studied by using a combination of Cyclic Voltammetry (CV) and Electrochemical Quartz Crystal Microbalance (EQCM). 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. The composition of the films determined by EDS supports the assumption of the deposition process which is based on the EQCM studies. The obtained results indicate the role of sulfamic acid as a comlexing agent. The concentration of 20 mM of sulfamic acid and the growing potential of - 0.9 V were found to be the most suitable conditions for deposition of Copper-Selenium layers towards CIGS thin film solar cell application.

1. Introduction

$Cu(In_{1-x}Ga_x)Se_2$ (CIGS) is one of the most promising semiconductor materials that can be used to prepare the thin film solar cells [1, 2]. Several techniques have been employed to prepare CIGS thin films [3-9]. Among these techniques, one-step electrodeposition seems to be the most suitable one because it is economic, simple, and allows to deposit over large surface areas. In this technique, in order to improve deposition process, sulfamic acid can be added into solution as a complexing agent. Because the formation of CIGS is generally taken via the formation of Cu-Se phases, the deposition of Cu-Se system is the most interested problem [10]. In a previous study on the deposition of CIGS compound carried out by Cyclic Voltammetry technique (CV) [11], we have observed the significant changes of the

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voltammograms after introducing sulfamic acid with different concentration, especially in case of Cu-Se binary system. However, due to the fact that the CV technique only provides the deposition current during scanning, the mechanism of the process is not really clear. In this work, by using a combination of Cyclic Voltammetry (CV) and Electrochemical Quartz Crystal Microbalance (EQCM), which measures the effective deposited mass simultaneously with the deposition current, we focused on the effect of sulfamic acid as a complexing agent on the formation of Cu-Se compounds via the quantity so called the equivalent atomic mass (M/z) grown at the gold EQCM sensor during electrodeposition at varying potentials and constant potentials. So far to our knowledge, this was the first time that the EQCM technique was carried out in Vietnam. The value of the equivalent atomic mass is very important because it provides clearly information about the redox process, i.e. the elements taking part the process as well as the deposit stoichiometry. The values of M/z deduced from scanning process indicate the evolution of process while those deduced from electrostatic process is more convincing. In addition, EDS composition of the obtained samples was used to support the EQCM results.

2. Experimetal

Cyclic Voltammetry (CV) and Electrochemical Quartz Crystal Microbalance (EQCM) were carried out in a combination system including an Autolab PGSTAT30 potentiostat/galvanostat and a KSV QCM-Z500 instrument (Hanoi University of Science, Vietnam). The QCM-Z500 was used as an EQCM when it was equipped with an electrochemical chamber.

The potentiostat connected to the EQCM via a three-electrode configuration where the reference electrode was Ag/AgCl 3M KCl electrode, the counter electrode was one of the Pt electrode poles and the working electrode was one side of the quartz crystal (the Au film). The quartz crystal was 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 cm² projected area of the Au electrode.

Each measurement used 2 ml electrolyte which contained deionized water, 20 mM $CuCl_2$, 20 mM H_2SeO_3, 350 mM LiCl as supporting agent, 25 mM KHP (Potassium Hydrogen Phthalate) and H_3SNO_3 (sulfamic acids) with the concentration ranging from 0 mM to 40 mM as the complexing agents. Before measurements, the electrolytes were dissolved by ultrasonic for 5 minutes.

All the cyclic voltammograms and microgravimetry scans were measured at a speed of 10 mV/s and were scanned first to the negative direction. The electrodepositions (ED) were carried out potentiostatically at the potentials of - 0.3 V, - 0.6 V and - 0.9 V for 20 minutes. The concentration of the films grown by ED was determined by Energy Dispersive Spectroscopy (EDS).

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

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

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

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

$$\Delta Q = \frac{Fz}{M}\Delta m \tag{2}$$

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 [12, 13], one obtains

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

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)

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

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.

3. Results and discussion

3.1. Potential scanning process

Fig 1 shows the equivalent atomic mass (M/z) obtained at the gold EQCM during scanning electrodeposition potential at three conditions which are different in concentration of sulfamic acids.

In the absence of sulfamic acid, at the potential of - 0.2 V, the M/z value is close to 63 g/mol, corresponding to the redox process of copper described by equation:
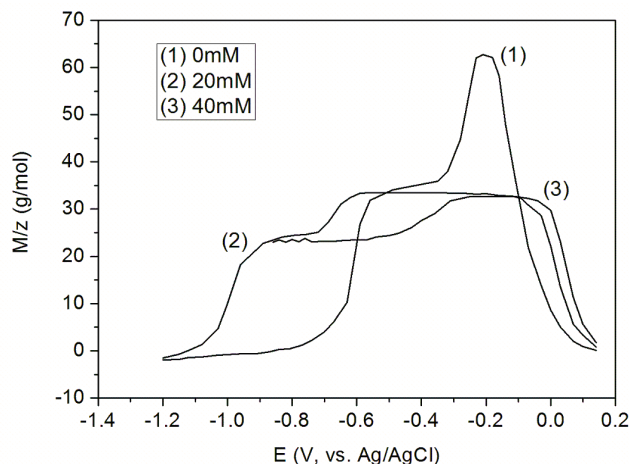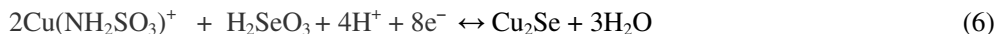
$$CuCl_2^- + e^- \leftrightarrow Cu^0 + 2Cl^-$$
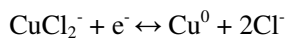
Fig.1. The equivalent atomic mass (M / z) obtained at the gold EQCM in solutions containing $CuCl_2$, H_2SeO_3 and sulfamic acid with different concentration.
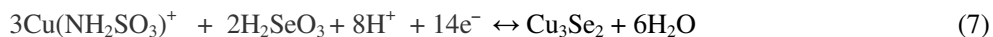
As the Se reduction begins, the value of M / z reduces to value of about 35 g/mol and then decreases slightly until the potential of - 0.6 V. At - 0.6 V the M / z plot decreases abruptly to zero, indicating that at the potential more negative than - 0.6 V, no deposit is formed. Concerning the value of M / z 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 / z 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 / z should result from one of the following reactions:

$$Cu(NH_2SO_3)^+ + H_2SeO_3 + 4H^+ + 6e^- \leftrightarrow CuSe + 3H_2O \tag{5}$$

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

$$2Cu(NH_2SO_3)^+ + H_2SeO_3 + 4H^+ + 8e^- \leftrightarrow Cu_2Se + 3H_2O \tag{6}$$

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

$$3Cu(NH_2SO_3)^+ + 2H_2SeO_3 + 8H^+ + 14e^- \leftrightarrow Cu_3Se_2 + 6H_2O \tag{7}$$

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

It means that in the region from - 0.7 V to - 1.0 V, the formation of Cu-Se compounds has been 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 imppoible to determine value of M/z. The second phenomena should relate to a mass loss process. Marlot et al. has observed a mass loss process when they studied the deposition of Cu-Se by using a rotating EQCM [14]. 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:

$$2CuSe + 2H^+ + 2e \leftrightarrow Cu_2Se + H_2Se \tag{8}$$

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

3.2. Potentiostatically 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 2a, 2b and 2c 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 2a, the Δf vs. ΔQ plots exhibit the case of a stationary growth, i.e. they are linear over the all deposition time. It is very 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 takes place at - 0.6 V, we can see in Fig 2b 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. 1 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.
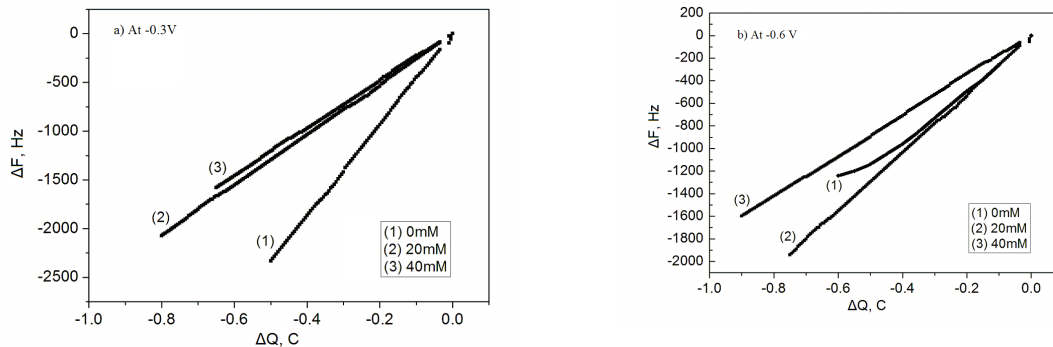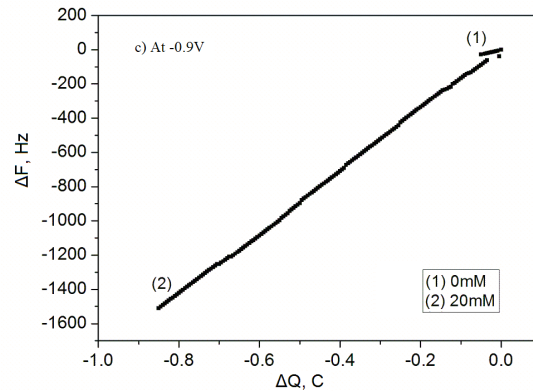
Fig.2. The Δf vs. ΔQ plots measured in solutions containing different concentration of sulfamic acid at the potentiostatic deposition: a) - 0.3V, b) - 0.6V and c) - 0.9V.

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 1 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.

3.3. Composition of the potentialstatic deposition samples

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 decribing the EDS composition of the samples grown by potentialstatic deposition.

Table 1: The x value decribing 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

Based on the assumption of the deposition mechanism mentioned in the sessions 3.1 and 3.2, we can explain the varying of the composition at different growing conditions.

For the solution not containing sulfamic acid, at potential of - 0.3 V, the deposited layer is Cu rich compound because in this case, the reduction of Cu dominates. At potential of - 0.6 V, the ratio of

Cu: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 potentials of - 0.3 V and - 0.6 V, the Cu-Se stoichiometry is $CuSe_{1.8}$ which is in accordance with the M/z value of 35 g/mol. It is interesting to note that, at 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. 5-7) forming different Cu-Se phases. Considering that the best stoichiometry of CIGS film is $Cu(In_{1-x}Ga_x)Se_2$, 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 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.

4. Conclusions

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 The composition of the films determined by EDS are in agreement with the assumption which is based on the EQCM studies. The obtained results indicate the role of sulfamic acid as a comlexing agent. The concentration of 20 mM of sulfamic acid and the potential of - 0.9 V were found to be the most suitable conditions for deposition of Copper-Selenium layers towards CIGS thin film solar cell application.

Acknowledgments

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