

Compositional Analysis of Electrodeposited Cu-Se Compound Semiconductor Thin Films Using Combined Voltammetry and Flow-Electrochemical Quartz Crystal Microgravimetry

Wooju Lee, Seonghan Jeong, Noseung Myung,* Krishnan Rajeshwar,† and Chi-Woo Lee‡

Department of Applied Chemistry, Konkuk University, Chungju, Chungbuk 380-701, Korea. *E-mail: myung@kku.ac.kr

†Department of Chemistry & Biochemistry, University of Texas at Arlington, Arlington, TX 76109-0065, U.S.A.

‡Department of Advanced Materials Chemistry, Korea University, 2511 Sejongro, Sejong 339-700, Korea

Received May 31, 2013, Accepted July 5, 2013

Key Words : Copper selenide, Electrodeposition, EQCM, Compositional analysis

The ternary compound semiconductor CuInSe_2 (CIS) has attracted great interest due to its unique properties and wide applications. Especially, it is one of the most attractive photovoltaic materials due to the high absorption coefficient and stability.¹⁻⁵ In that sense, the study of the Cu-Se binary system is important since it is an intermediate or precursor for the preparation of CIS.²⁻⁶ In addition, it is also an important material for photovoltaic solar cells and for Schottky diodes.⁶⁻⁸ Therefore Cu-Se has been synthesized using various methods including solvothermal, photochemical, chemical vapor deposition and electrodeposition.^{3,9}

Electrodeposition has been extensively used for the deposition of inorganic semiconductors because of its simplicity, low cost, mild conditions for film growth, and intrinsic ability to control the growth rate and composition of the film.^{10,11} However, it is well known that this method suffers from the contamination of target material with impurities (e.g., contamination of CdSe with free Se).¹⁰⁻¹² Considering the effect of composition on the properties of semiconductor, it is important to control composition as well as to develop methods for the compositional analysis of thin films.¹⁰⁻¹³ We have previously reported on compositional analysis of electrodeposited semiconductor thin films (such as CdSe, Bi_2Se_3 and Bi_2Te_3) using combined voltammetry with electrochemical quartz crystal microgravimetry (EQCM).¹⁰⁻¹² In this report, we describe a new electroanalytical route using combined EQCM and stripping voltammetry for the compositional analysis of Cu-Se thin films electrodeposited at different potentials.

Experimental Section

All chemicals including copper sulfate (99%), selenium dioxide (99.8%), sodium sulfate (99%) and sulfuric acid (98%) were from Aldrich. They were used as received without further purification.

For voltammetry, an EG&G Princeton Applied Research (PAR) 263A instrument equipped with Model M250/270 electrochemistry software was used. For EQCM, a Seiko EG&G Model QCA 917 instrument consisting of an oscillator module (QCA 917-11), a 9 MHz AT-cut gold-coated quartz

crystal (geometric area, 0.2 cm^2) working electrode, a Pt counter electrode and a Ag/AgCl/3 M NaCl reference electrode was used.

The flow-EQCM has been used for the deposition and compositional analysis of CdSe and Bi_2Te_3 thin films. Details of the flow-EQCM setup are given elsewhere.¹⁰ For flow-EQCM experiments, an EG&G Princeton Applied Research Model 273A system was used and frequency changes were displayed on a Kipp and Zonen Model BD111 single pen chart recorder. A Gilson Minipuls 3 peristaltic pump was used to deliver solution to the flow-EQCM system and a Valco Model 6-way slider valve equipped with 0.15 mm i.d. tubing was employed to switch and inject solutions at a nominal flow rate of 0.28 mL/min. The flow rate and a cell volume (about 0.5 mL) were enough for the deposition of thin films considering the concentration of Cu^{2+} and Se^{4-} ions.

Results and Discussion

Electrodeposited Cu-Se thin films contain Cu, Se and Cu_2Se depending on the electrodeposition condition. Therefore, stripping voltammograms for the individual species were obtained using the electrodeposited Se, Cu_2Se and Cu. Figure 1(a) shows a voltammogram with frequency changes during the cathodic stripping of the electrodeposited Se film in 0.1 M Na_2SO_4 blank electrolyte. The Se film was pre-electrodeposited at -0.4 V for 60 s using 10 mM SeO_2 in 0.1 M H_2SO_4 . The peak at $\sim -0.8 \text{ V}$ is clearly due to the reduction of Se to Se^{2-} supported by the frequency increase as well as previous reports.^{11,14} Electrochemistry of selenium has been extensively described in a recent review paper.¹⁵ To differentiate the peak due to Se reduction from that arising from Cu_2Se reduction, Cu-Se film was electrodeposited at -0.1 V using 0.1 M H_2SO_4 containing 10 mM SeO_2 and 5 mM CuSO_4 . After the free Se was removed from the film by applying -0.7 V for 100 s in 0.1 M Na_2SO_4 blank electrolyte,^{11,14} the film was subjected to a cathodic scan in 0.1 M Na_2SO_4 blank electrolyte as shown in Figure 1(b). In this study, 0.1 M Na_2SO_4 was used as a blank electrolyte instead of 0.1 M H_2SO_4 to avoid interference from the hydrogen

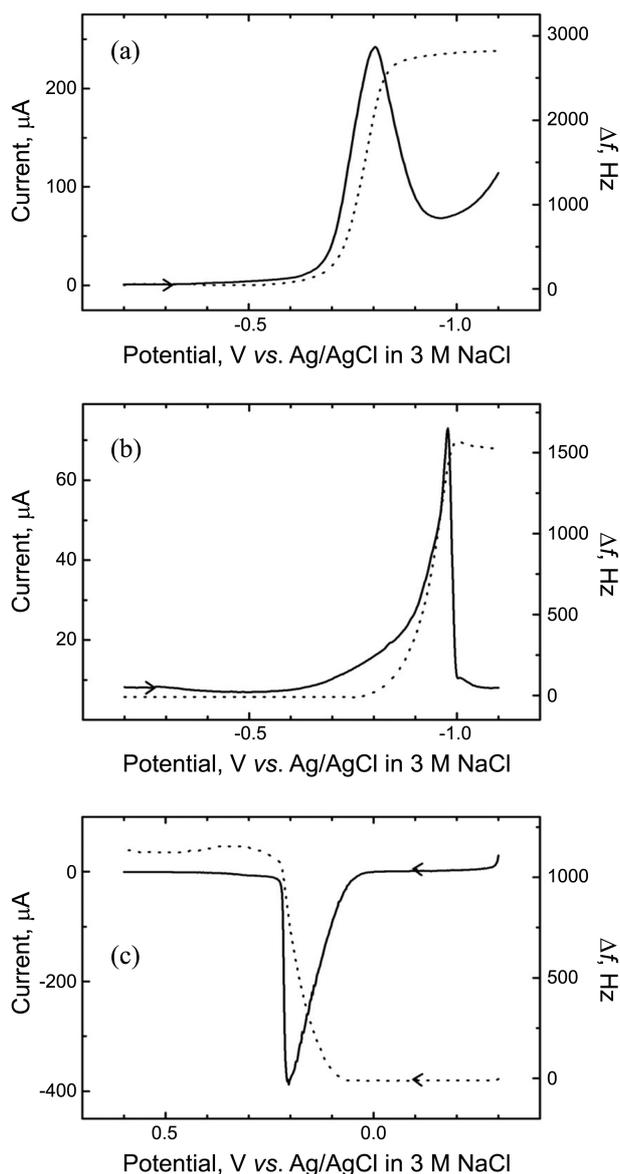


Figure 1. Linear sweep voltammograms (solid line) and the corresponding EQCM frequency changes (dashed line) for the stripping of (a) Se, (b) Cu_2Se and (c) Cu in 0.1 M Na_2SO_4 solution. Scan rate: 10 mV/s.

evolution. Unlike Figure 1(a), a cathodic peak was observed at -0.98 V which is assigned to the reduction of Cu_2Se to Cu and Se^{2-} . This behavior is in good agreement with previous results.^{11,14} Electrodeposition of Cu_2Se was confirmed by the cathodic photocurrent of the film upon light illumination, which is consistent with p-type semiconductor behavior. In order to further assign the peak at -0.98 V in Figure 1b, the number of electrons (n) transferred during the reduction was calculated from the slope of charge-frequency plot:¹⁰

$$Q = -(nFk/M)\Delta f \quad (1)$$

In Eq. (1), Q is charge, F is Faraday constant, k is sensitivity factor, M is molar mass and Δf is frequency changes. The n value obtained from the slope was found to be 1.9, which clearly shows that the peak is due to reduction of

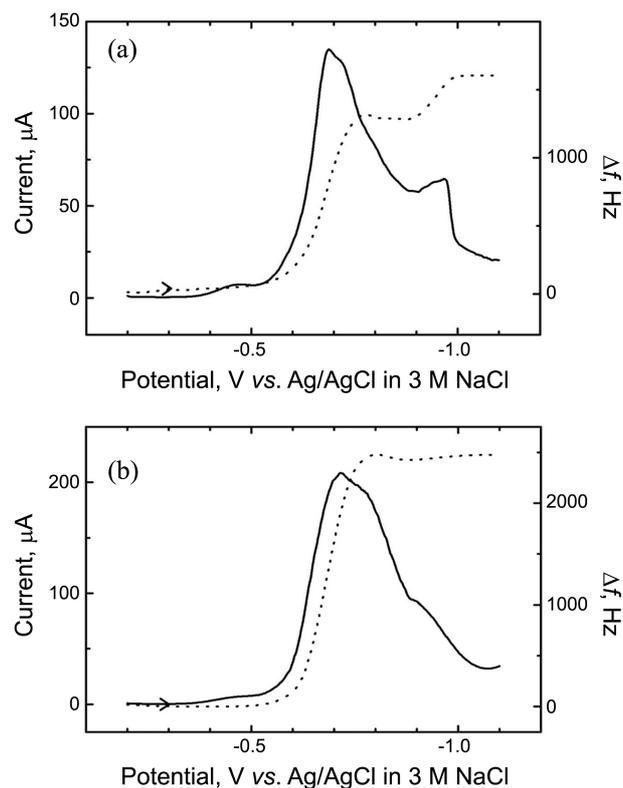


Figure 2. Linear sweep voltammograms (solid line) and the corresponding EQCM frequency changes (dashed line) for the cathodic stripping of Cu-Se thin films in 0.1 M Na_2SO_4 solution. Thin films were electrodeposited at (a) -0.1 V and (b) -0.3 V for ~ 4 kHz using 0.1 M H_2SO_4 containing 10 mM SeO_2 and 5 mM CuSO_4 . Scan rate: 10 mV/s.

Cu_2Se :



Next, a pre-electrodeposited Cu film was anodically stripped in 0.1 M Na_2SO_4 blank electrolyte (Figure 1(c)). The Cu film was electrodeposited at -0.1 V for 60 s using 0.1 M H_2SO_4 containing 5 mM CuSO_4 . The peak at $+0.2$ V is assigned to Cu oxidation to Cu^{2+} in 0.1 M Na_2SO_4 electrolyte.

The data in Figure 2 were obtained during the cathodic stripping of Cu-Se thin films electrodeposited at -0.1 V (Figure 2(a)) and -0.3 V (Figure 2(b)), respectively. Both films were electrodeposited using 0.1 M H_2SO_4 containing 10 mM SeO_2 and 5 mM CuSO_4 until the EQCM frequency decreased by ~ 4 kHz. The film deposited at -0.1 V resulted in a voltammogram with two distinctive peaks at -0.7 V and -0.98 V, which are due to the successive reduction of free Se and Cu_2Se to Se^{2-} and $\text{Cu} + \text{Se}^{2-}$, respectively. On the other hand, Cu-Se films deposited at -0.3 V showed only one large peak at -0.7 V, which corresponds to the reduction of free Se to Se^{2-} . These data clearly demonstrate that the film composition is sensitive to the electrodeposition potential.

Now, the composition of electrodeposited Cu-Se thin films (free Cu, free Se and Cu_2Se) was determined using combined stripping voltammetry and flow-EQCM. Figure 3

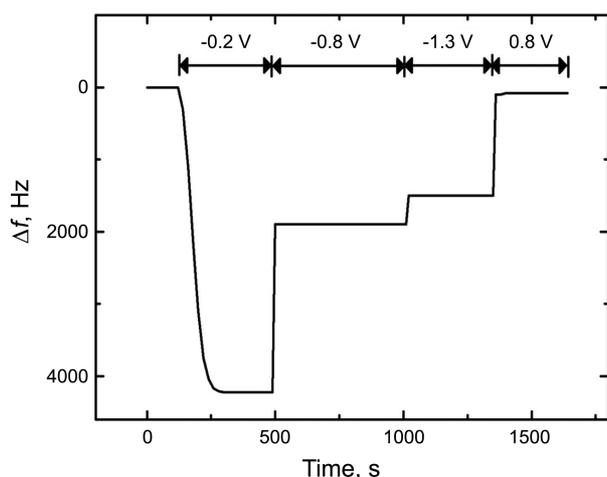


Figure 3. EQCM frequency (mass) changes during the electrodeposition and stripping steps. Electrolytes for electrodeposition and stripping were same as in Figure 2.

contains frequency changes at different potentials applied during the electrodeposition and stripping stages. First, Cu-Se films were electrodeposited at different potentials (for example, -0.2 V in Figure 3) using the electrolyte used to prepare Cu-Se thin films in Figure 2. When the EQCM frequency changed by ~ 4 kHz, the electrolyte was changed to 0.1 M Na_2SO_4 blank electrolyte to prevent further increase of film thickness and a series of potentials were applied to the electrode. Free Se content was first determined from the frequency changes when a cell potential was switched to -0.8 V. When the frequency did not change further, another potential step to -1.3 V was applied to determine the content of Se in Cu_2Se based on the 2:1 compound stoichiometry. Then the total Cu (free Cu + Cu in Cu_2Se) was determined *via* anodic stripping at $+0.8$ V and free Cu content was calculated from the difference between total Cu and Cu in Cu_2Se . The results are shown in Figure 4.

Figure 4 again clearly demonstrates that the composition of electrodeposited Cu-Se thin films is sensitive to the electrodeposition potential. All quantitative data were based

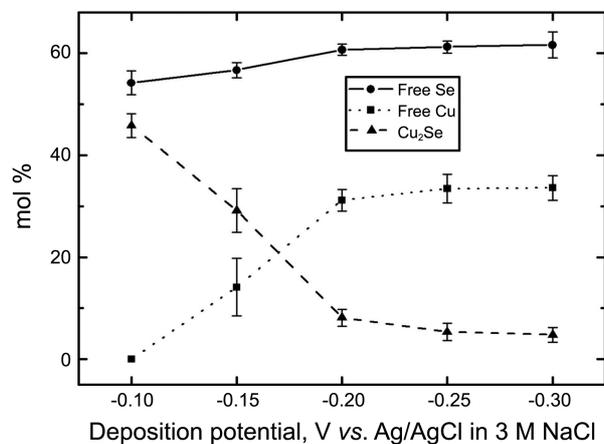


Figure 4. Compositional variation of Cu-Se films electrodeposited at different potentials and determined by the procedure described in Figure 3. The error bars denote one standard deviation.

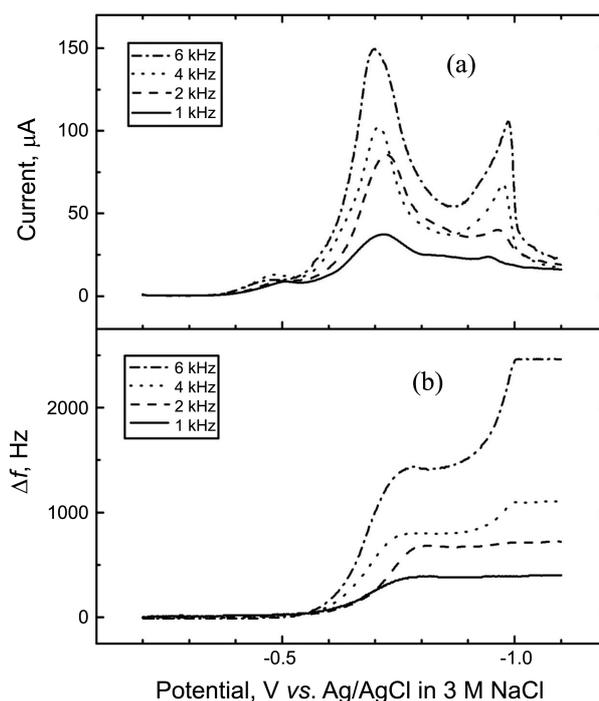


Figure 5. (a) Linear sweep voltammograms and (b) the corresponding EQCM frequency changes for Cu-Se films in 0.1 M Na_2SO_4 . Cu-Se films were electrodeposited at -0.1 V for 1–6 kHz using 0.1 M H_2SO_4 containing 10 mM SeO_2 and 5 mM CuSO_4 . Scan rate: 10 mV/s.

on the frequency changes during the stripping step, and reproducibility was checked by running five replicates. As seen in the figure, the content of Cu_2Se decreases with potential decrease and the content of free Cu shows a reverse trend. On the other hand, the free Se content of the film is not substantially affected by electrodeposition potential and is almost constant at potentials investigated. The amounts of frequency change are proportional to the thickness of electrodeposited thin films. It can be estimated that film thickness varies between 20–50 nm depending on the composition when frequency changed by ~ 4 kHz considering the densities of Cu, Se and Cu_2Se .¹⁶

Interestingly enough, the film composition was dependent on the deposition time (thickness of the film). Cu-Se films with different thickness were electrodeposited at -0.1 V using a 0.1 M H_2SO_4 containing 10 mM SeO_2 and 5 mM CuSO_4 . The content of free Se, free Cu and Cu_2Se in the electrodeposited film was determined by the procedure described in Figure 3. During the first 1 kHz (less than ~ 10 nm thick), the film almost consists of free Se and free Cu. However, the amount of Cu_2Se increased as the film thickness increases from 1 kHz to 6 kHz or deposition time increases as seen in Figure 5. This behavior reveals that post-chemical reaction between two elements results in the formation of Cu_2Se binary compound and this trend is in good agreement with a previous report.¹³

In summary, a novel method which is species selective for the compositional analysis of electrodeposited Cu-Se semiconductor films was developed using combined voltammetry

and flow-EQCM. The amounts of free Se and Se in Cu₂Se were obtained from the frequency changes at constant potentials of -0.8 V and -1.3 V, respectively. Potential steps to -0.8 V and -1.3 V were employed to reduce free Se to Se²⁻ and Cu₂Se to Cu + Se²⁻, respectively. Resultant total Cu was anodically stripped at +0.8 V and the free Cu content was calculated using the difference in frequency changes observed during the stripping of total Cu and Se in Cu₂Se. The results showed that the amounts of free Se, free Cu and the targeted Cu₂Se varied with deposition potential as well as film thickness.

Acknowledgments. This work was financially supported by the National Research Foundation of Korea (NRF-2010-0029164, NRF-2012R1A2A1A03055900 and NRF-2011-0021386).

References

1. Mishra, K. K.; Rajeshwar, K. *J. Electroanal. Chem.* **1989**, *271*, 279.
 2. Carbonnelle, P.; Lamberts, L. *J. Electroanal. Chem.* **1992**, *340*, 53.
 3. Kemell, M.; Ritala, M.; Saloniemi, H.; Leskela, M.; Sajavaara, T.; Rauhala, E. *J. Electrochem. Soc.* **2000**, *147*, 1080.
 4. Caballero-Briones, F.; Palacios-Padros, A.; Sanz, F. *Electrochim. Acta* **2011**, *56*, 9556.
 5. Chung, Y.; Lee, C.-H. *J. Electrochem. Sci. Tech.* **2012**, *3*, 95.
 6. Riveros, G.; Henriquez, R.; Cordova, R.; Schrebler, R.; Dalchiele, E. A.; Gomez, H. *J. Electroanal. Chem.* **2001**, *504*, 160.
 7. Lippkow, D.; Strehblow, H.-H. *Electrochim. Acta* **1998**, *43*, 2131.
 8. Chaudhri, M.; Vohra, A.; Chakarvarti, S. K. *Mater. Sci. Eng. B* **2008**, *149*, 7.
 9. Kou, H.; Jiang, Y.; Li, J.; Yu, S.; Wang, C. *J. Mater. Chem.* **2012**, *22*, 1950.
 10. (a) Ham, S.; Jeon, S.; Lee, U.; Park, M.; Paeng, K.-J.; Myung, N.; Rajeshwar, K. *Anal. Chem.* **2008**, *80*, 6724. (b) Myung, N.; Jun, J. H.; Ku, H. B.; Chung, H.-K.; Rajeshwar, K. *Microchem. J.* **1999**, *62*, 15.
 11. Ham, S.; Jeon, S.; Park, M.; Choi, S.; Paeng, K.-J.; Myung, N.; Rajeshwar, K. *J. Electroanal. Chem.* **2010**, *638*, 195.
 12. Myung, N.; Wei, C.; Rajeshwar, K. *Anal. Chem.* **1992**, *64*, 2701.
 13. Marlot, A.; Vedel, J. *J. Electrochem. Soc.* **1999**, *146*, 177.
 14. Choi, S.; Chae, Y.; Ham, S.; Lee, W.; Myung, N.; Rajeshwar, K. *J. Phys. Chem. C* **2012**, *116*, 20146.
 15. Saji, V. S.; Lee, C.-W. *RSC Adv.* **2013**, *3*, 10058.
 16. Gulay, L.; Daszkiewics, M.; Strok, O.; Pietraszko, A. *Chem. Met. Alloys* **2011**, *4*, 200.
-