

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

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The ternary compound semiconductor  $\text{CuInSe}_2$  (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.<sup>1-5</sup> 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.<sup>2-6</sup> In addition, it is also an important material for photovoltaic solar cells and for Schottky diodes.<sup>6-8</sup> Therefore Cu-Se has been synthesized using various methods including solvothermal, photochemical, chemical vapor deposition and electrodeposition.<sup>3,9</sup>

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.<sup>10,11</sup> 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).<sup>10-12</sup> 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.<sup>10-13</sup> We have previously reported on compositional analysis of electrodeposited semiconductor thin films (such as CdSe,  $\text{Bi}_2\text{Se}_3$  and  $\text{Bi}_2\text{Te}_3$ ) using combined voltammetry with electrochemical quartz crystal microgravimetry (EQCM).<sup>10-12</sup> 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.

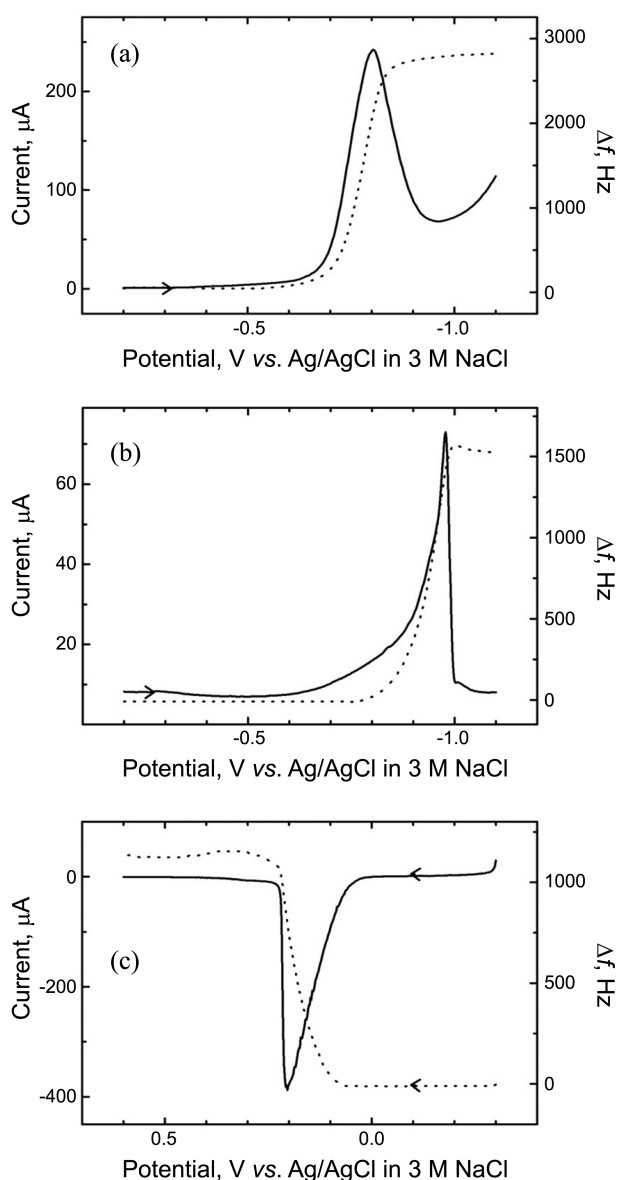
For voltammetry, an EG&G Princeton Applied Research (PAR) 263A instrument equipped with Model M250/270 electrochemistry software was used. For EQCM, a Seiko EG&G Model QCA 917 instrument consisting of an oscillator module (QCA 917-11), a 9 MHz AT-cut gold-coated quartz

crystal (geometric area,  $0.2 \text{ cm}^2$ ) 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  $\text{Bi}_2\text{Te}_3$  thin films. Details of the flow-EQCM setup are given elsewhere.<sup>10</sup> 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  $\text{Cu}^{2+}$  and  $\text{Se}^{4-}$  ions.

### Results and Discussion

Electrodeposited Cu-Se thin films contain Cu, Se and  $\text{Cu}_2\text{Se}$  depending on the electrodeposition condition. Therefore, stripping voltammograms for the individual species were obtained using the electrodeposited Se,  $\text{Cu}_2\text{Se}$  and Cu. Figure 1(a) shows a voltammogram with frequency changes during the cathodic stripping of the electrodeposited Se film in 0.1 M  $\text{Na}_2\text{SO}_4$  blank electrolyte. The Se film was pre-electrodeposited at  $-0.4 \text{ V}$  for 60 s using 10 mM  $\text{SeO}_2$  in 0.1 M  $\text{H}_2\text{SO}_4$ . The peak at  $\sim -0.8 \text{ V}$  is clearly due to the reduction of Se to  $\text{Se}^{2-}$  supported by the frequency increase as well as previous reports.<sup>11,14</sup> Electrochemistry of selenium has been extensively described in a recent review paper.<sup>15</sup> To differentiate the peak due to Se reduction from that arising from  $\text{Cu}_2\text{Se}$  reduction, Cu-Se film was electrodeposited at  $-0.1 \text{ V}$  using 0.1 M  $\text{H}_2\text{SO}_4$  containing 10 mM  $\text{SeO}_2$  and 5 mM  $\text{CuSO}_4$ . After the free Se was removed from the film by applying  $-0.7 \text{ V}$  for 100 s in 0.1 M  $\text{Na}_2\text{SO}_4$  blank electrolyte,<sup>11,14</sup> the film was subjected to a cathodic scan in 0.1 M  $\text{Na}_2\text{SO}_4$  blank electrolyte as shown in Figure 1(b). In this study, 0.1 M  $\text{Na}_2\text{SO}_4$  was used as a blank electrolyte instead of 0.1 M  $\text{H}_2\text{SO}_4$  to avoid interference from the hydrogen

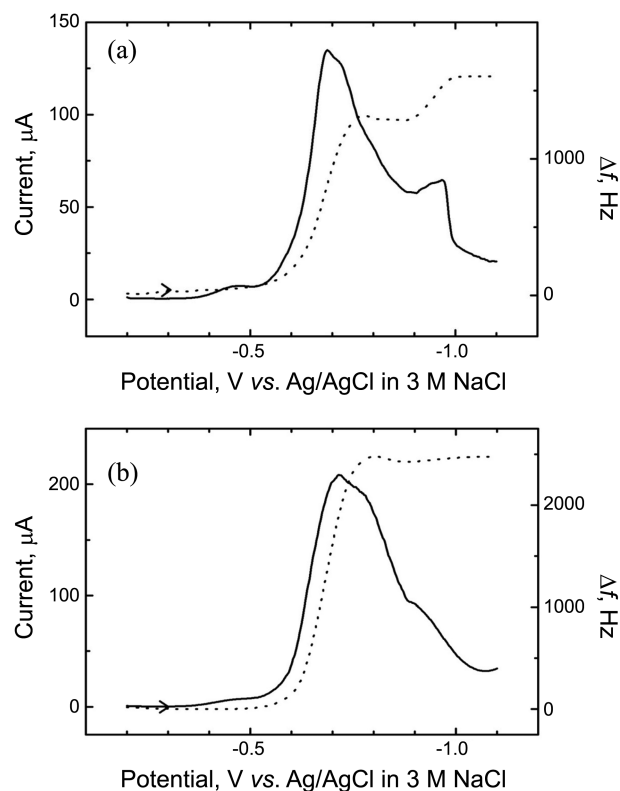


**Figure 1.** Linear sweep voltammograms (solid line) and the corresponding EQCM frequency changes (dashed line) for the stripping of (a) Se, (b)  $\text{Cu}_2\text{Se}$  and (c) Cu in 0.1 M  $\text{Na}_2\text{SO}_4$  solution. Scan rate: 10 mV/s.

evolution. Unlike Figure 1(a), a cathodic peak was observed at  $-0.98$  V which is assigned to the reduction of  $\text{Cu}_2\text{Se}$  to Cu and  $\text{Se}^{2-}$ . This behavior is in good agreement with previous results.<sup>11,14</sup> Electrodeposition of  $\text{Cu}_2\text{Se}$  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:<sup>10</sup>

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

In Eq. (1),  $Q$  is charge,  $F$  is Faraday constant,  $k$  is sensitivity factor,  $M$  is molar mass and  $\Delta f$  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  $\text{Na}_2\text{SO}_4$  solution. Thin films were electrodeposited at (a)  $-0.1$  V and (b)  $-0.3$  V for  $\sim 4$  kHz using 0.1 M  $\text{H}_2\text{SO}_4$  containing 10 mM  $\text{SeO}_2$  and 5 mM  $\text{CuSO}_4$ . Scan rate: 10 mV/s.

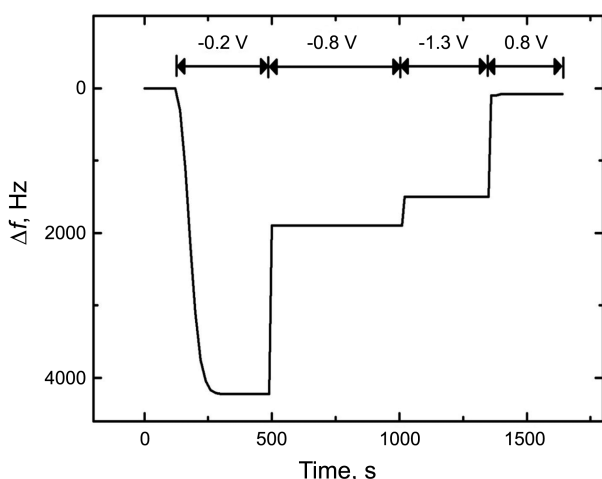
$\text{Cu}_2\text{Se}$ :



Next, a pre-electrodeposited Cu film was anodically stripped in 0.1 M  $\text{Na}_2\text{SO}_4$  blank electrolyte (Figure 1(c)). The Cu film was electrodeposited at  $-0.1$  V for 60 s using 0.1 M  $\text{H}_2\text{SO}_4$  containing 5 mM  $\text{CuSO}_4$ . The peak at  $+0.2$  V is assigned to Cu oxidation to  $\text{Cu}^{2+}$  in 0.1 M  $\text{Na}_2\text{SO}_4$  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  $\text{H}_2\text{SO}_4$  containing 10 mM  $\text{SeO}_2$  and 5 mM  $\text{CuSO}_4$  until the EQCM frequency decreased by  $\sim 4$  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  $\text{Cu}_2\text{Se}$  to  $\text{Se}^{2-}$  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  $\text{Se}^{2-}$ . These data clearly demonstrate that the film composition is sensitive to the electrodeposition potential.

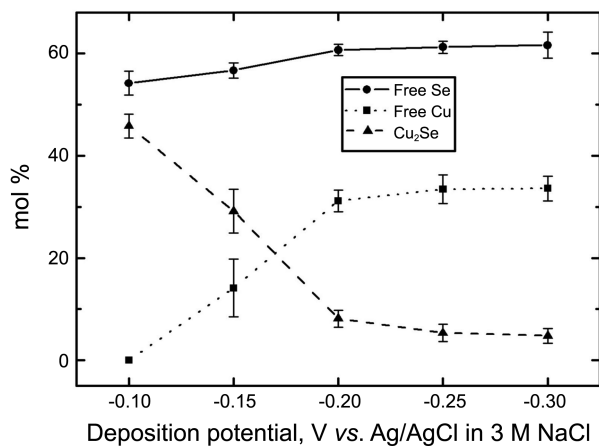
Now, the composition of electrodeposited Cu-Se thin films (free Cu, free Se and  $\text{Cu}_2\text{Se}$ ) was determined using combined stripping voltammetry and flow-EQCM. Figure 3



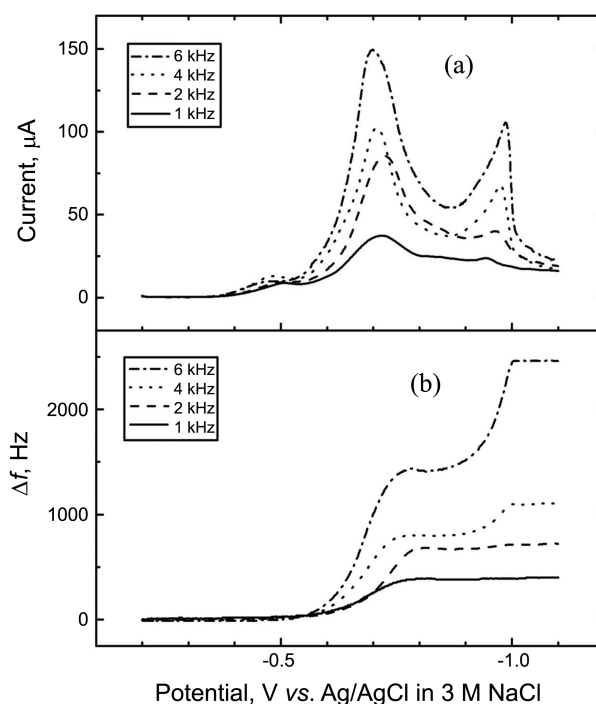
**Figure 3.** EQCM frequency (mass) changes during the electrodeposition and stripping steps. Electrolytes for electrodeposition and stripping were same as in Figure 2.

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  $\sim 4$  kHz, the electrolyte was changed to 0.1 M  $\text{Na}_2\text{SO}_4$  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  $\text{Cu}_2\text{Se}$  based on the 2:1 compound stoichiometry. Then the total Cu (free Cu + Cu in  $\text{Cu}_2\text{Se}$ ) was determined via anodic stripping at  $+0.8$  V and free Cu content was calculated from the difference between total Cu and Cu in  $\text{Cu}_2\text{Se}$ . 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  $\text{Na}_2\text{SO}_4$ . Cu-Se films were electrodeposited at  $-0.1$  V for 1–6 kHz using 0.1 M  $\text{H}_2\text{SO}_4$  containing 10 mM  $\text{SeO}_2$  and 5 mM  $\text{CuSO}_4$ . 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  $\text{Cu}_2\text{Se}$  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  $\sim 4$  kHz considering the densities of Cu, Se and  $\text{Cu}_2\text{Se}$ .<sup>16</sup>

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  $\text{H}_2\text{SO}_4$  containing 10 mM  $\text{SeO}_2$  and 5 mM  $\text{CuSO}_4$ . The content of free Se, free Cu and  $\text{Cu}_2\text{Se}$  in the electrodeposited film was determined by the procedure described in Figure 3. During the first 1 kHz (less than  $\sim 10$  nm thick), the film almost consists of free Se and free Cu. However, the amount of  $\text{Cu}_2\text{Se}$  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  $\text{Cu}_2\text{Se}$  binary compound and this trend is in good agreement with a previous report.<sup>13</sup>

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 Cu<sub>2</sub>Se 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 Se<sup>2-</sup> and Cu<sub>2</sub>Se to Cu + Se<sup>2-</sup>, 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 Cu<sub>2</sub>Se. The results showed that the amounts of free Se, free Cu and the targeted Cu<sub>2</sub>Se varied with deposition potential as well as film thickness.

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