Photoelectrochemical Deposition of CdZnSe Thin Films on the Se-Modified Au Electrode

Sunyoung Ham, Soyeon Jeon,[†] Ungki Lee,[†] Ki-Jung Paeng,[*] and Noseung Myung[†,*]

Department of Chemistry, Yonsei University, Wonju Campus, Wonju, Kangwon 220-710, Korea. *[*]E-mail: paengk@yonsei.ac.kr*
[†]Department of Applied Chemistry, Konkuk University, Chungju Campus, Chungju, Chungbuk 380-701, Korea
[*]E-mail: myung@kku.ac.kr
Received January 25, 2008

Photoelectrochemical deposition of CdZnSe thin films on the Se-modified Au electrode using electrochemical quartz crystal microgravimetry (EQCM) and voltammetry is described. Corrosion of pre-deposited Se electrodes by illumination at a fixed potential resulted in Se^{2-} species, which was manifest from the EQCM frequency changes. Se^{2-} species generated from the photocorrosion reacted with Cd^{2+} and Zn^{2+} ions in the electrolyte to form CdZnSe films on the Au electrode. The effect of electrolyte composition on the composition and band gap of CdZnSe films was studied in detail. Also, photoelectrochemistry, EDX, Raman spectroscopy were used for the characterization of CdZnSe thin films.

Key Words : Photoelectrochemistry, CdZnSe, Ternary semiconductor, EQCM

Introduction

Group 12-16 compound semiconductors are important in a wide spectrum of optoelectronic applications.[1] Especially, ternary compounds including cadmium zinc selenide (CdZnSe) have attracted much attention in the fields of solar cells due to their interesting properties of band gap modulation by composition.[2-6] For example, band gap values of CdZnSe ternary semiconductors can be varied from 1.7 eV (CdSe) to 2.7 eV (ZnSe) with composition.[2-4]

Different methods have been used for the synthesis of ternary compounds including vacuum techniques, chemical bath deposition and electrodeposition.[1-6] In particular, electrodeposition is a simple and cost-effective approach, which can conveniently modulate the composition of the thin films using electrolyte composition and deposition potentials.[1]

Photocorrosion reaction is detrimental to the long-term stability of the photoelectrode and can be prevented by a suitable redox couple.[7] As an extension to the previous studies,[8,9] we utilized photocorrosion reaction to synthesize ternary semiconductor CdZnSe thin films. Photoexcitation of the pre-deposited p-Se generates Se^{2-} under light illumination and thus generated Se^{2-} species react with Cd^{2+} and Zn^{2+} in electrolyte to result in CdZnSe. The composition as well as band gap of the film varies with electrolyte composition. This approach is validated using electrochemical quartz crystal microgravimetry (EQCM) and voltammetry.

Experimental

Details of the electrochemical instrumentation and the set-up for electrochemical quartz crystal microgravimetry (EQCM) are given elsewhere.[8,9] For voltammetry and film deposition, an EG&G Princeton Applied Research (PAR) 263A instrument equipped with Model M250/270 electro-

chemistry software was used. For EQCM, a Seiko EG&G Model QCA 917 instrument consisting of an oscillator module (QCA 917) and a 9 MHz AT-cut gold-coated quartz crystal (geometric area, 0.2 cm²) as a working electrode were used. A Pt wire served as a counter electrode and the reference electrode was Ag/AgCl/3 M NaCl.

Cadmium sulfate hydrate (purity 98+%), selenium dioxide (purity 99.8%), zinc sulfate heptahydrate (purity 99%), sodium sulfate (purity 99+%) and sulfuric acid (purity 98+%) were obtained from Aldrich. All chemicals were used as received.

Müller Elektronik-Optik halogen lamp was used as the light source. The light intensity measured on the electrode surface with the Newport 70260 radiant power meter combined with the 70268 probe was ~100 mW in all the experiments described below, and this value is uncorrected for cell reflection and electrolyte absorption losses. Raman spectra were measured using the 514 nm line of an Ar^+ ion laser (HORIBA-LABRAM) at room temperature. Film morphology and atomic composition of the electrodeposited Se and CdZnSe were studied by energy dispersive X-ray analyses (EDX) attached to a field emission scanning electron microscope (FESEM, JEOL 6700F). Interferometric reflectance spectra were obtained with an Ocean Optics R4000 spectrometer system equipped with a fiber optic probe and a W-halogen light source.

Results and Discussion

As a prelude to experiments on CdZnSe, the deposition and photoelectrochemical characteristics of selenium (Se) on the Au substrate were studied in detail to complement our earlier studies.[8,9] Figure 1A contains representative electrochemical, photo-electrochemical, and EQCM data for a polycrystalline Au electrode pre-modified with Se. Se was deposited by holding an Au electrode at −0.6 V for 120 s in
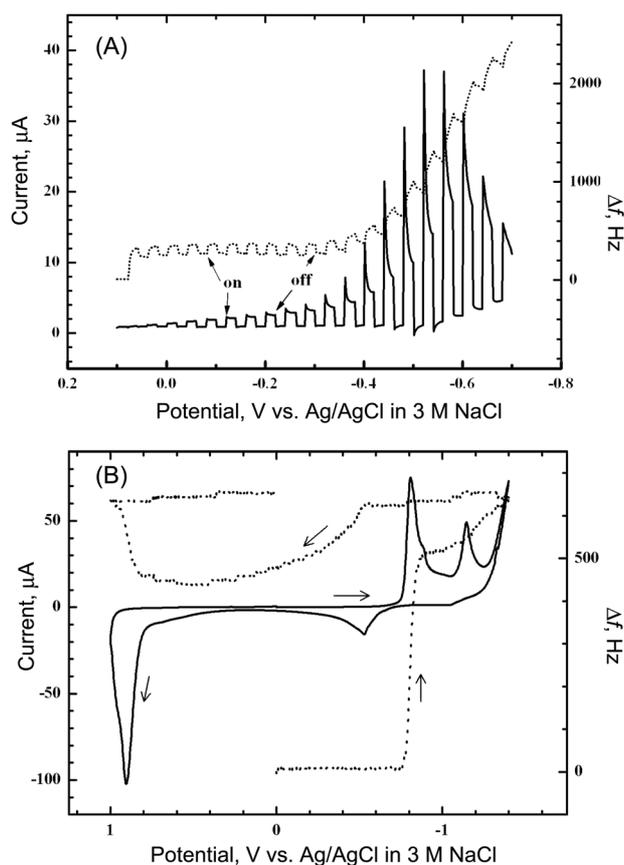
Figure 1. (A) Linear Sweep voltammogram (——) and the corresponding EQCM frequency changes (-----) for a Se modified Au electrode in 0.1 M Na$_2$SO$_4$. (B) Cyclic voltammogram (——) and the corresponding EQCM frequency changes (----) in the dark for a Se modified Au electrode in 0.1 M Na$_2$SO$_4$. Se was deposited by holding a Au electrode at −0.6 V for 120 s in 0.1 M Na$_2$SO$_4$ electrolyte containing 10 mM SeO$_2$.

0.1 M Na$_2$SO$_4$ electrolyte containing 10 mM SeO$_2$. The photocurrent transients (solid line) at −0.25 V in 0.1 M Na$_2$SO$_4$ electrolyte are cathodic, signaling that the Se as deposited on the Au surface is acting as a p-type semiconductor.[10] Apparently, the cathodic photocurrents are accompanied by the photocorrosion of Se to Se^{2-} which results in mass decreases (EQCM frequency *increases*, dashed line).

It should be noted that the electrode mass is regained when the light is switched off in each cycle showing that Se^0 re-deposits on the Au surface in the dark. To understand this, a combined cyclic voltammogram (CV) and EQCM is obtained for a Se modified Au electrode in 0.1 M Na$_2$SO$_4$. As shown in the Figure 1B, cathodic stripping of Se to Se^{2-} is accompanied by frequency increase (mass decrease) and as-generated Se^{2-} species re-deposit on the Au electrode again during the return scan (from ~ −0.5 V). This explains why photogenerated Se^{2-} is oxidized and re-deposited on the Au electrode in the dark. Again, frequency increase with an anodic peak at 0.8 V is due to the oxidation of Se to Se^{4+}.[11,12]

Under the light illumination, electrodeposited Se is stripped off due to the photocorrosion.[11,13] Figure 2 contains
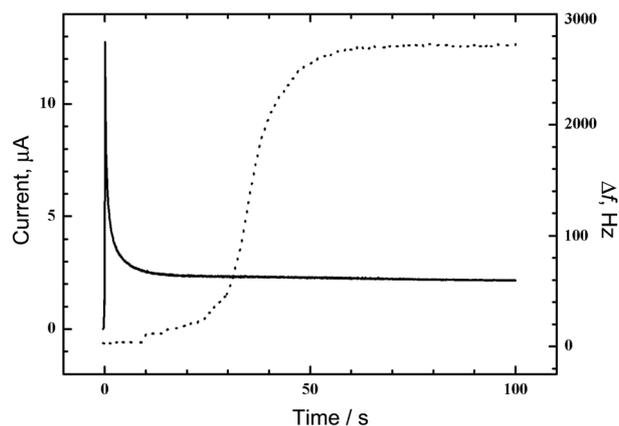
Figure 2. Current flow (——) and corresponding EQCM frequency change (-----) for a Se modified Au electrode in 0.1 M Na$_2$SO$_4$ at a fixed potential of −0.25 V with visible light illumination.

frequency changes during the light illumination on the Se modified Au electrode in 0.1 M Na$_2$SO$_4$ electrolyte at a fixed potential of −0.25 V. Again, Se was deposited by holding a Au electrode at −0.6 V for 120 s in 0.1 M Na$_2$SO$_4$ electrolyte containing 10 mM SeO$_2$. As shown in the figure, frequency increases (mass decrease) due to the photocorrosion of Se and photocorrosion is completed within ~50 s.

By contrast, addition of Cd^{2+} and/or Zn^{2+} to the electrolyte showed different frequency changes during the light illumi-
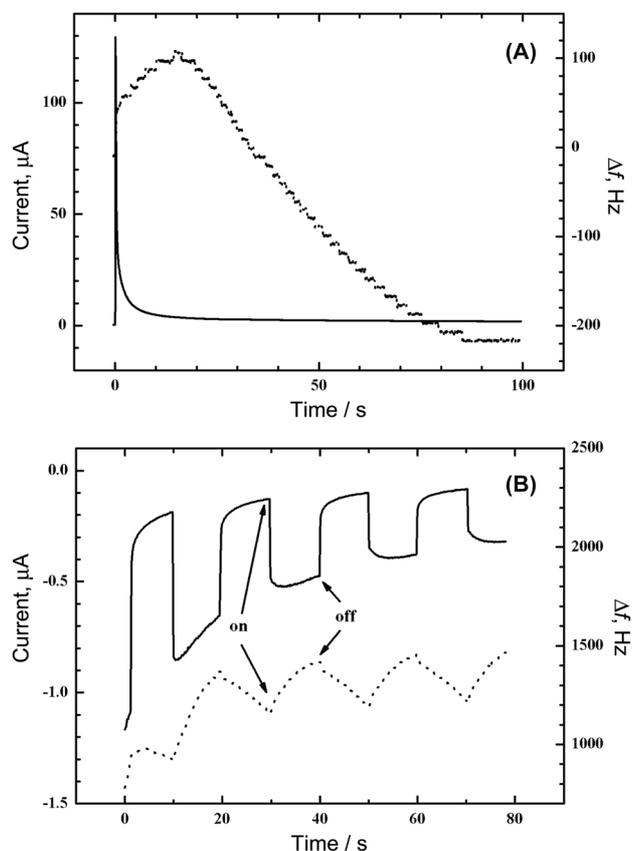
Figure 3. (A) As in figure 2 but with 30 mM CdSO$_4$. (B) Photocurrent transients (——) and the corresponding EQCM frequency change (-----) for a CdSe modified Au electrode in 0.1 M Na$_2$SO$_4$ at a fixed potential of −0.25 V.
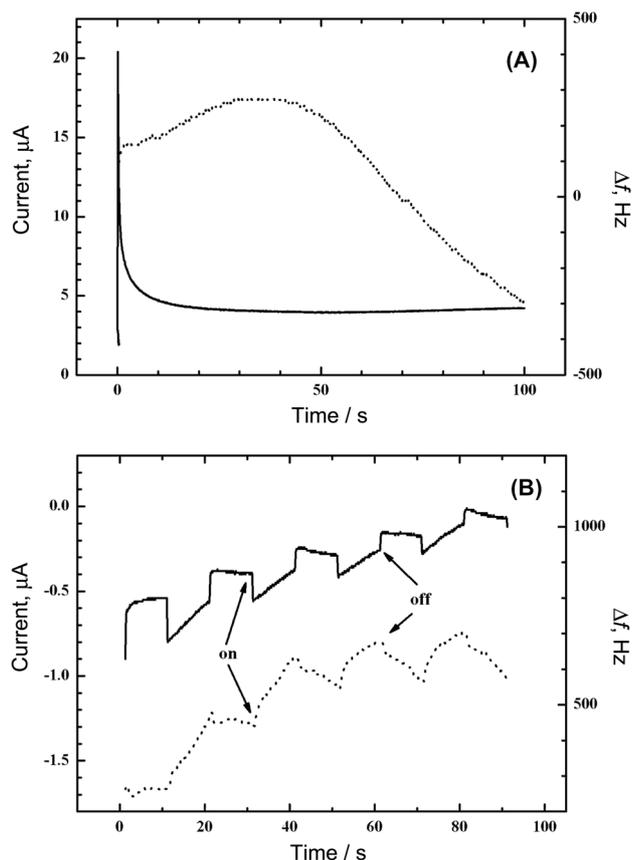
Figure 4. (A) As in figure 2 but with 50 mM ZnSO₄. (B) Photo-current transients (——) and the corresponding EQCM frequency change (-----) for a ZnSe modified Au electrode in 0.1 M Na₂SO₄ at a fixed potential of −0.25 V.

Figure 5. (A) As in figure 2 but with 1 mM CdSO₄ and 25 mM ZnSO₄. (B) Photocurrent transients (——) and the corresponding EQCM frequency change (-----) for a CdZnSe modified Au electrode in 0.1 M Na₂SO₄ at a fixed potential of −0.25 V.

nation. For example, irradiation on the Se modified Au electrode in 0.1 M Na₂SO₄ electrolyte containing 30 mM CdSO₄ at a fixed potential of -0.25 V results in frequency increase followed by a frequency decrease (Figure 3A). The frequency decrease resulted from the CdSe formation by the precipitation process:

$$Cd^{2+} + Se^{2-} \text{ (by photocorrosion)} \rightarrow CdSe \qquad (1)$$

Unlike the p-Se, the photocurrent is anodic as shown in figure 3B diagnosing that thus formed CdSe is n-type.[10,14-17] Again, the frequency changes systemically during the light on-off cycles as explained before (Figure 1A).

When electrolyte contains Zn^{2+} ions, similar frequency changes are observed during the light illumination on the Se modified Au electrode. Figure 4A contains chronoampero-metric and EQCM data for the Se modified Au electrode under the light illumination in 0.1 M Na₂SO₄ electrolyte containing 50 mM ZnSO₄ at a fixed potential of −0.25 V. The fixed potential of −0.25 V was selected since we observed cadmium and zinc deposition at more negative potentials in the dark. In the case of zinc, the frequency increases initially and starts to decrease, which implies the formation of ZnSe. Here, the frequency decreases from ~40 s, which is later than that of the CdSe case. We believe that this is due to the difference in solubility products of CdSe

($K_{sp} = 4.0 \times 10^{-35}$) and ZnSe ($K_{sp} = 1.0 \times 10^{-27}$).[18] Figure 4B shows that ZnSe formed by photocorrosion of Se and pre-cipitation reaction is n-type since photocurrent is anodic.[19] It should be mentioned that CdSe and ZnSe synthesized from photoelectrodeposition is not stable in Na₂SO₄ blank electrolyte, which can be seen from the decay in photo-current (Figures 3B and 4B). The photocorrosion can be inhibited using a suitable photoelectrolyte (redox couple).

Next, CdZnSe films are synthesized by the same approach described above. When Se modified Au electrode is sub-jected to photocorrosion in 0.1 M Na₂SO₄ electrolyte containing 1 mM CdSO₄ and 25 mM ZnSO₄ at a fixed potential of −0.25 V, CdZnSe films are synthesized as indicated from frequency decrease (Figure 5A). Also, photo-electrochemical behavior in Figure 5B is consistent with n-type behavior for the as-synthesized CdZnSe films.[3]

It is well known that band gap of CdZnSe is dependent on the film composition.[3,4] The composition of CdZnSe thin films synthesized by the approach developed here is deter-mined by EDX, Raman spectroscopy and UV reflectance spectroscopy. Figure 6A clearly shows that film composition and therefore band gap can be modulated by controlling electrolyte compositions. As shown in the figure, the ratio of Zn/Cd in films increases with the ratio of Zn/Cd in electrolyte. In addition, band gap has been modulated by the
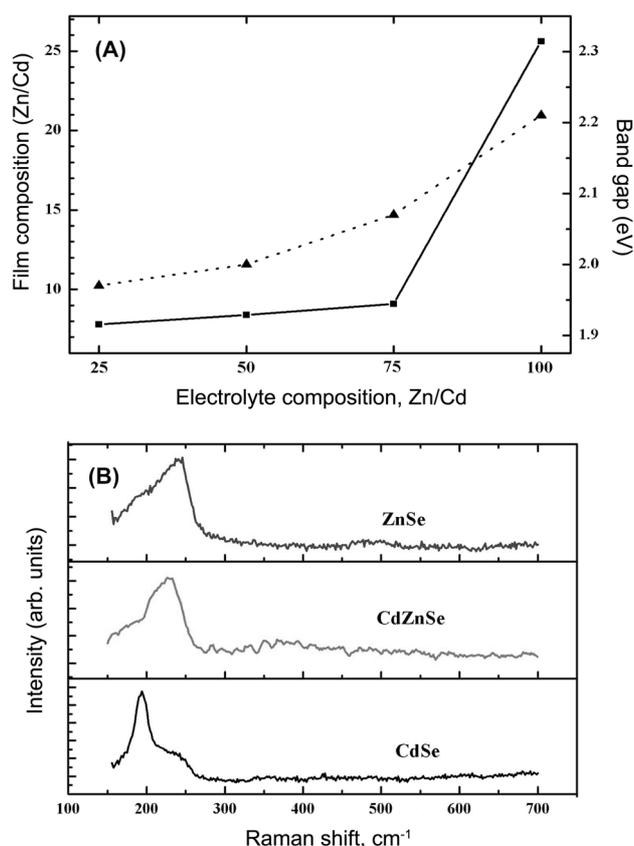
Figure 6. (A) Compositional (——) and band gap (-----) variations of as synthesized CdZnSe films with variations of electrolyte composition. (B) Raman spectra of CdSe, CdZnSe and ZnSe. CdSe and ZnSe were synthesized using conditions in figures 3A and 4A, respectively. CdZnSe was synthesized using conditions in figure 2 but with 1 mM CdSO$_4$ and 50 mM ZnSO$_4$.

electrolyte composition. Raman spectroscopy for as-synthe-sized films revealed peaks at 200 cm^{-1}, 250 cm^{-1} and 230 cm^{-1} for CdSe,[23] ZnSe[20-22,24] and CdZnSe,[6,25] respectively (Figure 6B). Their values are in well agreement with the literature values for these materials.

Conclusion

We have demonstrated a photoelectrochemical deposition of CdZnSe thin films using a Se modified Au electrode using a photocorrosion. Unlike previous studies on binary semiconductors, composition and band gap of ternary semi-conductors have been modulated by controlling composition of electrolytes. Also, we presented a new route for the synthesis of CdSe and ZnSe films using a photoelectro-chemical approach. Finally, EQCM combined with ampero-metry proved to be effective to study photoelectrochemical behavior of binary and ternary semiconductors.

References

1. (a) Rajeshwar, K. *Adv. Mater.* **1992**, *4*, 23. (b) Lee, J.; Kim, Y.; Kim, K.; Huh, Y.; Hyun, J.; Kim, H. S.; Noh, S. J.; Hwang, C. *Bull. Korean Chem. Soc.* **2007**, *28*, 1091.
2. (a) Krishnan, V.; Ham, D.; Mishra, K. K.; Rajeshwar, K. *J. Electrochem. Soc.* **1992**, *139*, 23. (b) Chae, D.; Seo, K.; Lee, S.; Yoon, S.; Shim, I. *Bull. Korean Chem. Soc.* **2006**, *27*, 762.
3. Natarajan, C.; Nogami, G.; Sharon, M. *Thin Solid Films* **1995**, *261*, 44.
4. Chandramohan, R.; Mahaligam, T.; Chu, J. P.; Sebastian, P. J. *Solar Energy Mater. Solar Cells* **2004**, *81*, 371.
5. Loglio, F.; Innocenti, M.; Pezzatini, G.; Foresti, M. L. *J. Elelctroanal. Chem.* **2004**, *562*, 117.
6. Kaschner, A.; Strassburg, M.; Hoffmann, A.; Thomsen, C.; Bartels, M.; Lischka, K.; Schikora, D. *Appl. Phys. Lett.* **2000**, *76*, 2662.
7. Licht, S. In *Semiconductor Electrodes and Photoelectrochemistry*; Licht, S., Ed.; Wiley: Weinheim, Germany, 2002; Vol. 6, p 325.
8. Ham, S.; Choi, B.; Paeng, K.; Myung, N.; Rajeshwar, K. *Electrochem. Commun.* **2007**, *9*, 1293.
9. Ham, S.; Paeng, K.; Park, J.; Myung, N.; Kim, S.; Rajeshwar, K. *J. Appl. Electrochem.* **2008**, *38*, 203.
10. Myung, N.; de Tacconi, N.; Rajeshwar, K. *Electrochem. Commun.* **1999**, *1*, 42.
11. Rabchynski, S. M.; Ivanou, D. K.; Streltsov, E. A. *Electrochem. Commun.* **2004**, *6*, 1051.
12. Myung, N.; Wei, C.; Rajeshwar, K. *Anal. Chem.* **1992**, *64*, 2701.
13. Streltsov, E. A.; Poznyak, S. K.; Osipovich, N. P. *J. Elelctroanal. Chem.* **2002**, *518*, 103.
14. Lade, S. J.; Uplane, M. D.; Lokhande, C. D. *Mater. Chem. Phys.* **2001**, *68*, 36.
15. Kazacos, M. S.; Miller, B. *J. Electrochem. Soc.* **1980**, *127*, 2378.
16. Rajeshwar, K.; Thompson, L.; Singh, P.; Kainthla, R. C.; Chopra, K. L. *J. Electrochem. Soc.* **1981**, *128*, 1744.
17. Choi, S.; Woo, D.; Myung, N.; Kang, H.; Park, S. *J. Electrochem. Soc.* **2001**, *148*, C569.
18. Hodes, G. *Chemical Solution Deposition of Semiconductor Films*; Marcel Dekker: New York, U.S.A., 2003; p 5.
19. Riveros, G.; Gümez, H.; Henriquez, R.; Schrebler, R.; Marotti, R. E.; Dalchiele, E. A. *Solar Energy Mater. Solar Cells* **2001**, *70*, 255.
20. Mahalingam, T.; Kathalingam, A.; Velumani, S.; Lee, S.; Sun, M. H.; Deak, K. Y. *J. Mater. Sci.* **2006**, *41*, 3353.
21. Murali, K. R.; Balasubramanian, M. *Mater. Sci. Eng. A* **2006**, *431*, 118.
22. Kumaresan, R.; Ichimura, M.; Arai, E. *Thin Solid Films* **2002**, *414*, 25.
23. Desnica-Frankovic, I. D.; Dubcek, P.; Buljan, M.; Furic, K.; Desnica, U. V.; Bernstorff, S.; Karl, H.; Großhans, I.; Stritzker, B. *Nucl. Instr. and Meth. B* **2005**, *238*, 302.
24. Lu, G.; An, H.; Chen, Y.; Huang, J.; Zhang, H.; Xiang, B.; Zhao, Q.; Yu, D.; Du, W. *J. Crystal Growth* **2005**, *274*, 530.
25. Schreder, B.; Materny, A.; Kiefer, W.; Kümmell, T.; Bacher, G.; Forchel, A.; Landwehr, G. *Solid State Chem.* **2000**, *114*, 435.