

Electrodeposition of Ternary CdZnS Semiconductor Thin Films Using a S-Modified Polycrystalline Au Electrode

Sunyoung Ham, Se Jin Cho, Ungki Lee[†], Soyeon Jeon[†], Jicheol Shin[†], Noseung Myung[†], and Ki-Jung Paeng*

Department of Chemistry, Yonsei University, Wonju Campus Wonju, Kangwondo 220-710, Korea

[†]Department of Applied Chemistry Konkuk University Chungju Campus Chungju, Chungbuk 380-701, Korea

(Received October 15, 2007 : Accepted November 8, 2007)

Abstract : This paper describes a two-step approach for the electrochemical deposition of CdZnS thin films on the polycrystalline Au electrode. Initially, an Au substrate is electrochemically modified with a sulfur layer. In the second step, the layer is electroreduced to S²⁻ in the electrolyte dosed with the requisite amount of Cd²⁺ and Zn²⁺ ions to generate CdZnS films in situ. This approach was validated using a combination of linear sweep voltammetry and electrochemical quartz crystal microgravimetry. Thus synthesized CdZnS thin films have different composition depending on the composition of electrolytes. CdZnS thin films are characterized by energy-dispersive X-ray analysis and Raman spectroscopy.

Keywords : Ternary semiconductor, CdZnS, Electrodeposition, EQCM, Voltammetry.

1. Introduction

Ternary semiconductors such as CdZnS and CdZnSe have been extensively studied due to the possibility of varying the bandgap with composition.¹⁻⁵⁾ Especially, CdZnS has been widely used as a wide-bandgap window material in heterojunction solar cells and found various applications in optical, electronic and optoelectronic devices.^{1,3-5)} The binary CdS and ZnS are n-type semiconductors that form a continuous series of solid solution with different stoichiometries and bandgap values ranging between 2.42 eV for CdS and 3.66 eV for ZnS.^{5,7)} Therefore, CdZnS thin films enable a tunable band gap region between 2.42 and 3.66 eV at normal temperature facilitates. Thin films of these materials are usually synthesized by molecular beam epitaxy,⁸⁾ electron beam evaporation⁹⁾ and chemical method.¹⁰⁾

Unlike the above-mentioned methods, electrodeposition has several advantages such as simplicity, low cost, ambient temperature operation and possibility of using large and irregular surfaces.¹¹⁾ Recently, a two-step method based on initial electrochemical modification of substrate with the chalcogen has been developed to avoid co-deposition of excess chalcogen element during the co-deposition of binary semiconductors.¹²⁻¹⁵⁾ Subsequent cathodic stripping of pre-deposited chalcogen in electrolytes containing a desired metal ion produces the binary semiconductor thin films on the electrode surface in situ. We and other authors have demonstrated this approach for the preparation of CdS,¹³⁾ CdSe,^{12,15)} CdTe¹⁶⁾ and ZnTe⁶⁾ thin films.

In this paper, we show that ternary semiconductor, CdZnS, can be electrosynthesized using the two-step approach. To

the best of our knowledge, this is the first time to demonstrate the approach for ternary semiconductor thin films. In the first step of the two-step approach, the gold substrate is electrochemically modified with sulfur layers. Next, these layers are electrochemically reduced to S²⁻ in an aqueous electrolyte medium dosed with the requisite amount of Cd²⁺ and Zn²⁺ ions to generate CdZnS thin films in situ. We shall describe below how the composition of films can be tuned by the composition of electrolytes. This approach is validated using a combination of voltammetry and electrochemical quartz crystal microgravimetry (EQCM). Thus synthesized films have been characterized with energy-dispersive X-ray analysis (EDX) and Raman spectroscopy.

2. Experimental section

Electrochemical instrumentation and the EQCM set-up are given in detail elsewhere.^{13,16)} An EG&G Princeton Applied Research (PAR) 263A instrument equipped with Model M 250/270 electrochemistry software was used for voltammetry as well as film deposition. For EQCM, a Seiko EG&G Model QCA 917 instrument consisting of an oscillator module (QCA 917-11) and a 9 MHz AT-cut gold-coated quartz crystal (geometric area, 0.2 cm²) working electrode, a Pt counter electrode, and a Ag/AgCl/3 M NaCl reference electrode, was used. All potentials are quoted with respect to this reference electrode. The cleanliness of the gold electrode was checked by cyclic voltammetry in 0.1 M H₂SO₄. The potential was cycled between -0.8 V and 0.7 V until the voltammetric and frequency signals were stable.

CdSO₄, Na₂S, ZnSO₄ and Na₂SO₄ were from Aldrich and used as received. All electrolytes were prepared with double-

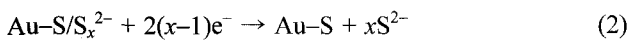
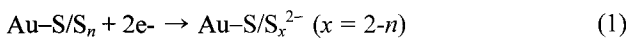
*E-mail: paeng@yonsei.ac.kr

distilled water (Corning Megapure) and purged with ultra-pure N₂.

Raman spectra were measured using the 514 nm line of an Ar⁺ ion laser (HORIBA - LABRAM) at room temperature. Film morphology and composition were obtained on a field emission scanning electron microscope (JEOL Model 6700F) equipped with an energy dispersive X-ray analysis (EDX) probe.

3. Results and Discussion

Electrodeposition and stripping of sulfur layers on gold electrodes have been extensively studied before and literatures are available.¹³ During the cathodic stripping of sulfur layers pre-deposited on a polycrystalline gold electrode, the sulfur layer is reduced in two steps:¹³



The Au-S submonolayer is reduced at potentials near the hydrogen reaction regime.¹³ Fig. 1(A) shows a combined linear sweep voltammetry (LSV) and EQCM data for the electroreduction of sulfur-modified polycrystalline Au electrode in 0.1 M Na₂SO₄ blank electrolyte. The sulfur layer was pre-deposited on Au by holding at -0.2 V for 5 min in 0.1 M Na₂SO₄ containing 10 mM Na₂S. The two waves in

figure 1(A) are assigned to Reactions (1) and (2), respectively.¹³ The figure clearly shows that frequency increase (mass decrease) during the electroreduction of sulfur to sulfide. Figures 1(B) and (C) contains LSV-EQCM data for a bare Au electrode 0.1 M Na₂SO₄ electrolyte containing 10 mM CdSO₄ and 10 mM ZnSO₄. Frequency changes indicate that cadmium (figure (B)) and zinc (figure (C)) deposition start at -0.8 V and -1.1 V, respectively. In order to use the two step approach, one condition should be met: reduction potentials for cadmium and zinc have to be more negative than the potential for sulfur reduction (sulfide generation). As shown in the figure, sulfur reduction occurs before cadmium and zinc reduction.

Unlike the case in fig. 1(A), wherein frequency is increased during the electroreduction of sulfur, frequency is now decreased (mass uptake) during the sulfur stripping when electrolyte contains Zn²⁺ and/or Cd²⁺ as shown in the Fig. 2. Fig. 2 (A) and (B) show formation of binary semiconductors, CdS and ZnS when 0.1 M Na₂SO₄ electrolytes contain 10 mM CdSO₄ or 10 mM ZnSO₄, respectively. In those cases, gold electrodes were pre-modified with sulfur layers as in fig. 1(A). New waves at -0.4 V (for ZnS) and -0.2 V (for CdS) can be assigned to the adsorption of Zn²⁺ and Cd²⁺ on the S-modified Au electrode.¹³ Also, waves at -0.8 V are originated from the sulfur reduction and formation of CdS, ZnS and CdZnS. Several authors have discussed the free energy gain upon the

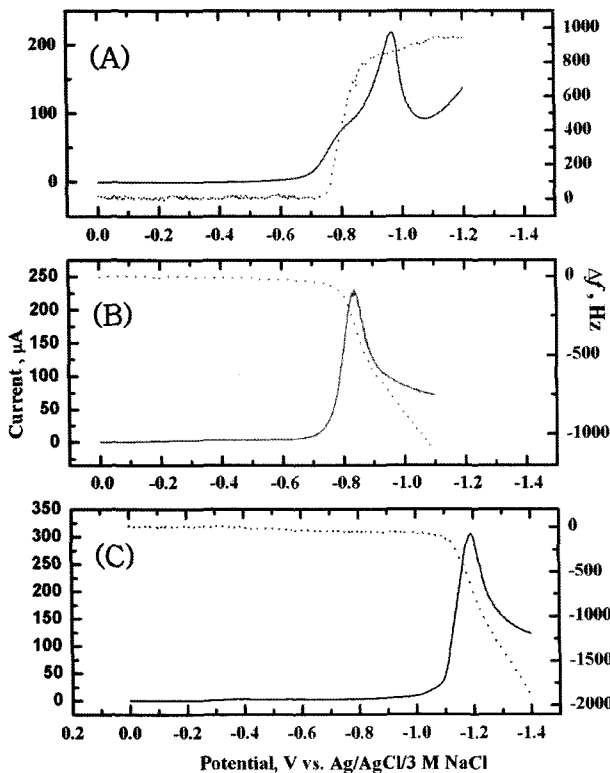


Fig. 1. Linear sweep voltammograms (—) and the corresponding frequency changes (---) for (A) the cathodic stripping of S in 0.1 M Na₂SO₄ solution, (B) deposition reduction of cadmium in 10mM CdSO₄ + 0.1 M Na₂SO₄ and (C) deposition of zinc using a 10mM ZnSO₄ + 0.1 M Na₂SO₄. Scan rate: 20 mV/s.

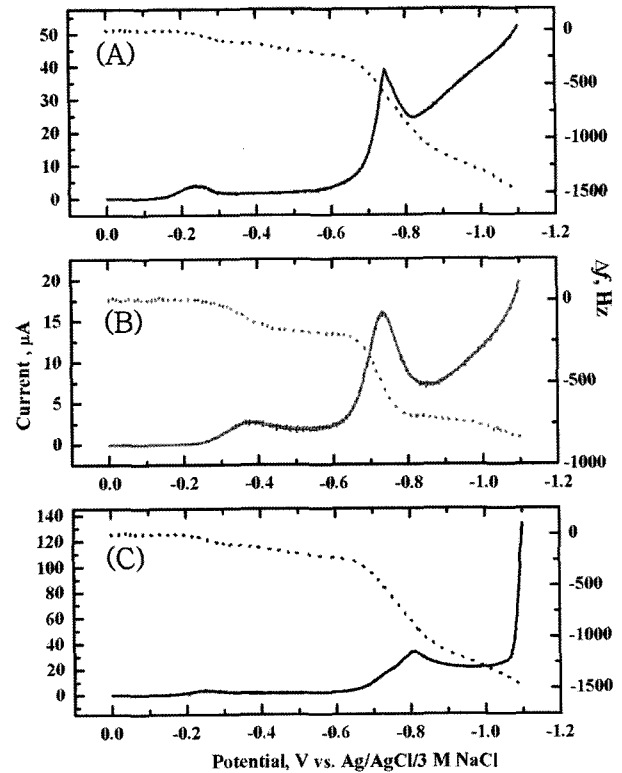


Fig. 2. Linear sweep voltammograms (—) and the corresponding frequency changes (---) during the electrosynthesis of (A) CdS (10mM CdSO₄), (B) ZnS (10 mM ZnSO₄) and (C) CdZnS (Cd : Zn = 1 mM : 50 mM) using a sulfur modified gold electrode. Scan rate: 20 mV/s.

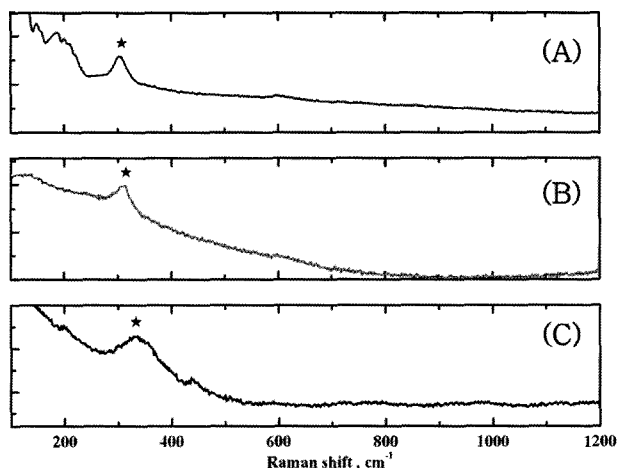


Fig. 3. Raman spectra of (A) CdS, (B) CdZnS and (C) ZnS. The films are synthesized using the conditions in figure 2.

Table 1. Compositional variations of Cd and Zn content in electrosynthesized CdZnS films along with their Raman peaks.

Cd : Zn in electrolyte	Cd : Zn in film	Raman peak
1 : 25	44.50 : 55.50	308 cm ⁻¹
1 : 50	40.34 : 59.66	313 cm ⁻¹
1 : 75	33.44 : 66.56	317 cm ⁻¹
1 : 100	29.29 : 70.71	323 cm ⁻¹

semiconductor formation.^{14,15}) Raman spectra of thus formed CdS and ZnS films will be discussed later (Fig. 3).

The same approach can be used for the synthesis of ternary semiconductor CdZnS. Fig. 2 (C) contains combined LSV-EQCM data for the electroreduction of sulfur-modified Au electrode in the 0.1 M Na₂SO₄ electrolyte containing 1 mM CdSO₄ and 50 mM ZnSO₄. Here, zinc concentration was significantly increased due to the difference in solubility product of CdS (8×10^{-7}) and ZnS (2×10^{-4}). In this case, the major peak which is assigned to the formation of CdZnS is shifted to more negative potential relative to the cases of CdS or ZnS synthesis. We used various concentrations of Zn²⁺ (from 25 mM to 100 mM) and similar LSV-EQCM data were obtained.

Synthesis of CdS, ZnS and CdZnS films are confirmed by laser Raman spectroscopy data, which are shown in fig. 3. In these experiments, films were electrosynthesized using experimental conditions as in fig. 2. The peaks at ~ 335 cm⁻¹ and 302 cm⁻¹ correspond to ZnS and CdS, respectively and they are very close to reported values.^{13,14}) As described by Ichimura and co-workers, Raman spectrum of CdZnS appears at wave number between that of CdS and ZnS.¹⁴) The peak at 313 cm⁻¹ is clearly diagnostic of CdZnS and it is evident that the two step approach can be used for synthesis of ternary semiconductors.¹⁴)

As summarized in Table 1, composition of electrolyte affected composition of the film. As the concentration ratio of Cd²⁺ to Zn²⁺ increases from 1 : 25 to 1 : 100 in the electrolytes, the Zn content in the film increased. This result implicates that film composition can be tuned by the variation of elec-

trolyte composition. As shown in the Table, the peak for CdZnS shifted to the peak for ZnS as the Zn concentration increased in the film.

4. Conclusions

CdS, ZnS and CdZnS films are electrochemically synthesized using a sulfur modified polycrystalline gold electrode by a two step method. Especially, control of Cd²⁺ and Zn²⁺ concentrations in electrolytes resulted in changes in composition of electrodeposited ternary semiconductor films. This result implicated that the two step method can be used for the preparation of ternary semiconductor films with different composition and band gaps. Further studies on photoelectrochemical properties and determination of band gaps of the films are currently under investigation.

Acknowledgement

This work was supported by a Korea Research Foundation Grant funded by the Korean Government (MOEHRD, Basic Research Promotion Fund) (KRF-2003-015-C00421). Two anonymous reviewers are thanked for their constructive criticisms.

References

1. Y. Akdogan, C. Uzum, O. Dag, N. Coombs, *J. Mater. Chem.*, **16**, 2048 (2006).
2. A. V. Krishnana, D. Ham, K. K. Mishra, K. Rajeshwar, *J. Electrochem. Soc.*, **139**, 23 (1992).
3. F. Loglio, M. Innocenti, G. Pezzatini, M. L. Foresti, *J. Electroanal. Chem.*, **562**, 117 (2004).
4. H. Lee, W.-C. Song, K.-J. Yang, Y.-S. Yoo, *Thin Solid Films*, **416**, 184 (2002).
5. P. Raji, K. Ramachandran, C. Sanjeeviraja, *J. Mater. Sci.*, **41**, 5907 (2006).
6. D. Han, S. Choi, S. Park, *J. Electrochem. Soc.*, **150**, C342 (2003).
7. M. Innocenti, S. Cattarin, M. Foresti, *Electrochim. Acta.*, **49**, 1327 (2004).
8. N. Samarth, H. Luo, N. Otsuka, *Appl. Phys. Lett.*, **54**, 2680 (1989).
9. R. Islam, D. Rao, *J. Mat. Sci. Lett.*, **13**, 1637 (1994).
10. R. Pandey, R. Rooz, *Semicond. Sci. Tech.*, **3**, 733 (1988).
11. K. Rajeshwar, *Adv. Mater.*, **4**, 23 (1992).
12. N. Myung, N.R. de Tacconi, K. Rajeshwar, *Electrochem. Commun.*, **1**, 42 (1999).
13. N. Myung, S. Ham, B. Choi, N. R. de Tacconi, K. Rajeshwar, *J. Electroanal. Chem.*, **574**, 367 (2005).
14. M. Ichimura, T. Furukawa, K. Shirai, F. Goto, *Mater. Lett.*, **33**, 51 (1997).
15. K. K. Mishra, K. Rajeshwar, *J. Electroanal. Chem.*, **273**, 169 (1989).
16. N. R. de Tacconi, K. Rajeshwar, *J. Electroanal. Chem.*, **444**, 7 (1998).
17. S.-J. Choi, D.-H. Woo, N. Myung, H. Kang, S.-M. Park, *J. Electrochem. Soc.*, **148**, C569 (2001).
18. S. Ham, B. Choi, N. Myung, N. R. de Tacconi, C. R. Chen-thamaraksan, K. Rakeshwar, Y. Son, *J. Electroanal. Chem.*, **601**, 77 (2007).
19. C. Natarajan, M. Sharon, C. Levi-Clement, M. Neumann-Spallart, *Thin Solid Films*, **237**, 118 (1994).