

Electrodeposition of CdS from Colloidal Sulfur Solutions Stabilized with Surfactants

H. Konno, J.-C. Lai, and M. Inagaki

Division of Materials Science and Engineering, Graduate School of Engineering, Hokkaido University, Sapporo, 060 Japan
Fax: 81-11-706-7114 e-mail ko@admac.hokudai.ac.jp

Abstract: Cathodic deposition of CdS film from the colloidal sulfur solutions prepared with CdSO_4 and $\text{Na}_2\text{S}_2\text{O}_3$ was examined. Different types of surfactant were screened to stabilize the colloidal solution, and anionic surfactants were found to be effective but other types were ineffective. The best results were obtained with sodium dodecylbenzenesulfonate (SDS). Reproducible deposition conditions to form CdS films of about $1\ \mu\text{m}$ were determined. As formed CdS film was zinc blend type (cubic structure) and the surface was slightly contaminated with sulfate-like compounds. They can be removed by vacuum annealing at 600°C for 5 min, but the structure changed and became wurtzite type (hexagonal structure) by 10 min heating.

Keywords: CdS film, cathodic deposition, sulfur sol, surfactant, XPS

1. Introduction

Electrochemical formation of CdS film has been studied as one of the promising methods. The film can be formed by cathodic polarization in solutions containing Cd(II) ions and colloidal sulfur [1,2], but the colloidal sulfur solutions are usually unstable due to flocculation. As a means to stabilize the solution, addition of gelatin is reported to be effective [2]. In the present work, different types of surfactant were screened to stabilize the colloidal sulfur solution, and the conditions to form CdS film by cathodic deposition with good reproducibility were surveyed.

2. Experimental

2.1 Screening of surfactants

Solutions of $0.05\ \text{mol dm}^{-3}$ $\text{Na}_2\text{S}_2\text{O}_3$ containing 0.002 - $0.0035\ \text{mol dm}^{-3}$ CdSO_4 were used. As-prepared solution was near neutral and, for screening, cationic, nonionic, or anionic surfactants were added to be 0.1 - $1.0\ \text{mass}\%$, then the solution pH was lowered with $1\ \text{mol dm}^{-3}$ H_2SO_4 to form sulfur sol from $\text{S}_2\text{O}_3^{2-}$ ions. Sulfur sol was quickly formed around pH 2. Surfactant has to be added to the solution before pH adjustment: the reverse procedure leads to unfavorable results even with useful ones.

2.2 Determination of the formation conditions of CdS film

Solution composition and pH were changed in the ranges as follows: $[\text{CdSO}_4] = 0.002$ - $0.01\ \text{mol dm}^{-3}$, $[\text{Na}_2\text{S}_2\text{O}_3] = 0.025$ - $0.1\ \text{mol dm}^{-3}$, and pH 1.2-3. ITO glass electrodes having sheet resistance of $10\ \Omega$ were used and additionally SnO_2 glass was used. It appeared that the conductivity of glass affected to the results, especially to thickness of deposits, but the glass composition didn't. Cathodic polarization was carried out at $26\pm 1^\circ\text{C}$ between -0.8 and $-0.9\ \text{V}$ vs. SCE (hereafter, vs. SCE is omitted) for 30-90 min, based on the cathodic polarization curves measured. Formed films were analyzed by XRD and XPS. Determination of accurate composition of the films by ICP-AES was attempted but abandoned, since it was difficult to decompose very small amount of CdS film appropriately.

2.3 Annealing of CdS film

Vacuum annealing of the formed films was carried out to modify and improve the quality of films. Specimens were vacuum-sealed in a Pyrex tube with a rotary pump and put in a furnace kept at 600°C for 5 or 10 min, then quickly cooled to ambient temperature.

3. Results and discussion

3.1 Screening of surfactants

In Table 1, typical results of screening are summarized. It is clear that cationic and nonionic surfactants cannot stabilize sulfur sol. Further, soluble hydrocarbons such as cyclodextrin were also ineffective. Only anionic surfactants are effective, and the best results were obtained with sodium dodecylbenzenesulfonate (SDS), when added at 0.5 - $1\ \text{mass}\%$. When the solution pH was around 2, only trace amounts of precipitate were observed even after 7 day standing.

Stability of the solution was markedly affected by solution pH. After 3 day standing of $0.0035\ \text{mol dm}^{-3}$ CdSO_4 - $0.05\ \text{mol dm}^{-3}$ $\text{Na}_2\text{S}_2\text{O}_3$ - $0.5\ \text{mass}\%$ SDS solution, large amounts of precipitate were observed at pH 1.2 and small amounts at pH 3, whereas precipitate was trace amounts at around pH 2. Low pH enhances the decomposition of thiosulfate ions to sulfur leading to quick precipitation. The reason of instability at pH 3, however, is not simple: there may be many factors and it is difficult to determine which is controlling the system, since the solution composition is complex due to the decomposition of thiosulfate ions. The solution of $0.0035\ \text{mol dm}^{-3}$ CdSO_4 - $0.1\ \text{mol dm}^{-3}$ $\text{Na}_2\text{S}_2\text{O}_3$ was also examined but precipitation started on the second day even at $1\ \text{mass}\%$ SDS. Therefore, practically $\text{Na}_2\text{S}_2\text{O}_3$ concentration should be around $0.05\ \text{mol dm}^{-3}$.

It is reasonable to consider that anionic surfactants adsorb with hydrophobic side on negatively charged sulfur sol [3] and increase surface charge, leading to stabilization. There was a tendency for the stabilizing ability of surfactant to increase with increasing the length of hydrocarbon chain when the structure is equivalent. For example, 1-octanesulfonic acid requires much higher concentration than 1-dodecanesulfonic acid to attain similar stabilization (Table 1). Further, it was

Table 1 Stability of the sulfur sol formed in a $0.0035 \text{ mol dm}^{-3} \text{ CdSO}_4$ - $0.05 \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_3$ solution containing different surfactants.

Type	Surfactant	Concentration / mass%	pH	Time until the start of precipitation / h
Cationic	Hexadecyltrimethylammonium chloride $[\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3]\text{Cl}$	0.10 - 0.75	1.8 - 2.4	0.5 - 1
Nonionic	2-(2-Butoxyethoxy)ethanol $\text{CH}_3(\text{CH}_2)_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$	0.10 - 0.75	1.9 - 2.3	4 - 12
Anionic	Sodium dodecylsulfate $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$	0.10 - 0.75	1.9 - 2.4	24 - 36
	Sodium <i>n</i> -hexadecylsulfate $\text{CH}_3(\text{CH}_2)_{15}\text{OSO}_3\text{Na}$	0.10	1.8 - 2.2	24 - 36
	1-Octanesulfonic acid sodium salt $\text{CH}_3(\text{CH}_2)_7\text{SO}_3\text{Na}$	0.10 - 0.75	1.8 - 2.4	24 - 48
	1-Dodecanesulfonic acid sodium salt $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_3\text{Na}$	0.05 - 0.10	1.8 - 2.3	24 - 48
	Sodium 4- <i>n</i> -octylbenzenesulfonate $\text{CH}_3(\text{CH}_2)_7\text{C}_6\text{H}_4\text{SO}_3\text{Na}$	0.10 - 0.80	1.9 - 2.3	4 - 12
	Sodium dodecylbenzenesulfonate $\text{C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{SO}_3\text{Na}$	0.10 - 0.45	1.9 - 2.4	36 - 48
			0.50 - 1.00	2.0 - 2.3

found that there was no relation between the critical micelle concentration of surfactant (CMC) and the stabilizing ability. For example, CMC of sodium 4-*n*-octylbenzenesulfonate is 15 mmol dm^{-3} at 40°C [4] and it was rather ineffective, while 1-octanesulfonic acid sodium salt was effective but CMC is 160 mmol dm^{-3} at 40°C [4] (Table 1).

3.2 Formation of CdS films

Cathodic current on a ITO glass electrode was found to increase below -0.5 V by cyclic voltammetry in the 3 day aged solution of $0.0035 \text{ mol dm}^{-3} \text{ CdSO}_4$ - $0.05 \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_3$ - 0.5 mass\% SDS (pH ca. 2 with H_2SO_4). Hereafter, this solution is used unless otherwise mentioned. By 1 h potentiostatic electrolysis, visible yellow films were formed below -0.8 V . As shown in Fig. 1, XRD patterns of the film revealed that zinc blend type CdS (cubic structure) is formed under these conditions, but below -0.85 V metallic Cd was also deposited. Formed CdS films were always smooth and adhesive. From the peak intensity of ITO underneath, the film was found to grow with deposition time, but even at -0.82 V longer electrolysis than 60 min led to metal deposition.

The effect of CdSO_4 and $\text{Na}_2\text{S}_2\text{O}_3$ concentrations on the structure of deposits obtained by 1 h electrolysis at -0.82 V is shown in Figs. 2 and 3, where other factors were kept constant as mentioned above. The results indicate that $\text{Na}_2\text{S}_2\text{O}_3/\text{CdSO}_4$ mole ratio should be larger than 10 to avoid the metal deposition. Accordingly, CdSO_4 concentration should be about $0.004 \text{ mol dm}^{-3}$ at the most. This limits the rate of film formation, but in order to increase CdSO_4 concentration $\text{Na}_2\text{S}_2\text{O}_3$ concentration must be increased and it leads to the unstable solution as described in 3.1.

Composition of the films was attempted to measure by ICP-AES after dissolving them into acid solutions but the results for sulfur content were so scattered that it was unable to determine. Only Cd(II) content was obtained within a reasonable error, and it suggested that thickness of the film formed at -0.82 V for 60 min was about $1 \mu\text{m}$.

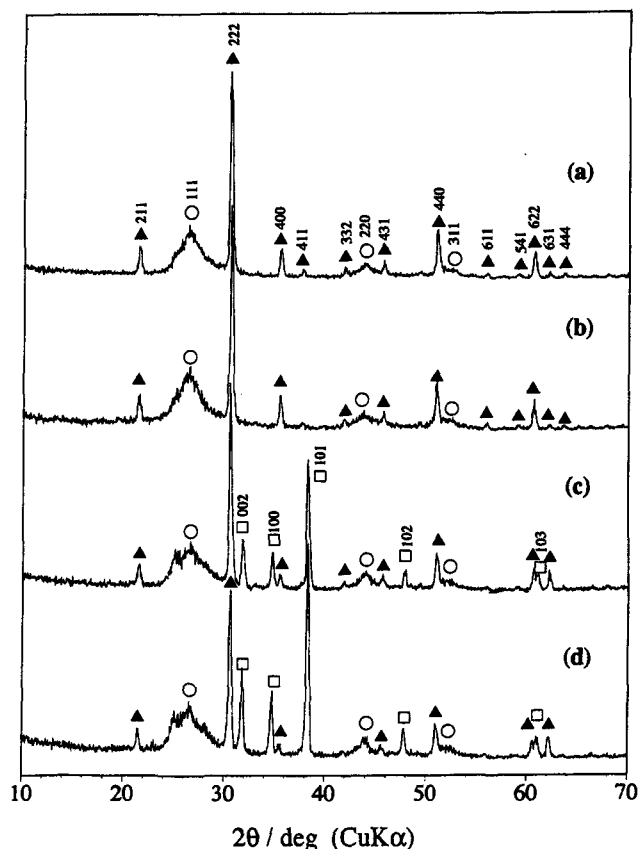


Fig. 1 XRD patterns of the film formed at different cathode potentials: (a) -0.80 V , (b) -0.82 V , (c) -0.85 V , and (d) -0.90 V . ○ CdS(cubic), □ Cd, and ▲ ITO.

From XPS spectrum of Cd $3d_{5/2}$ electrons and Cd $M_4N_{4,5}N_{4,5}$ Auger spectrum for as-formed film, Auger parameter was calculated at 785.8 eV . The value is slightly smaller than 786.6 eV reported for CdS [5]. Further, XPS spectrum of S 2p

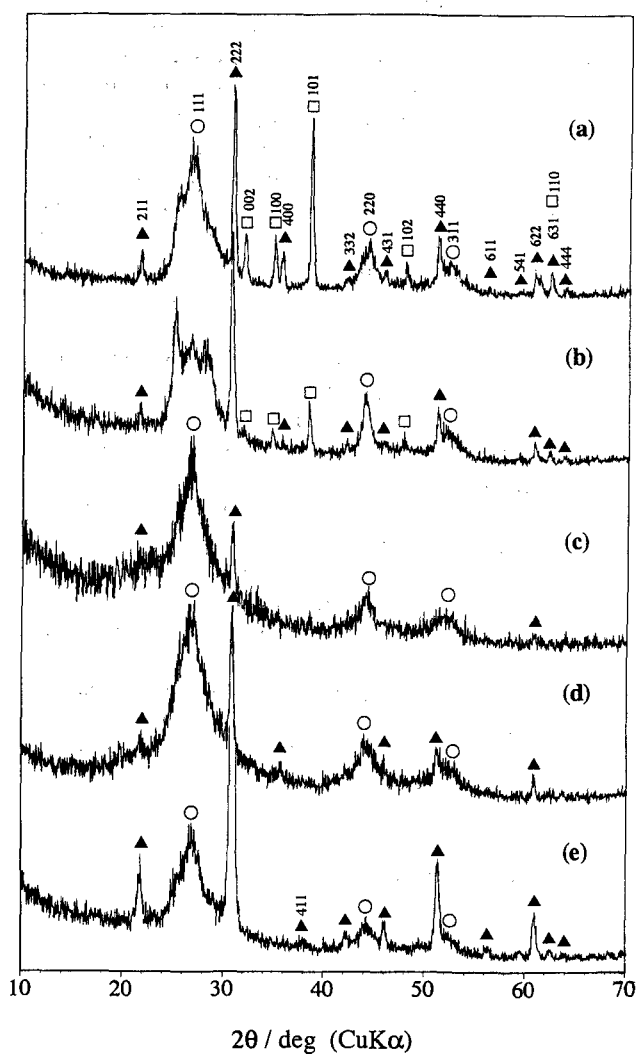


Fig. 2 Effect of CdSO₄ concentration: (a) 0.010, (b) 0.0050, (c) 0.0035, (d) 0.0025, and (e) 0.0020 mol dm⁻³. ○ CdS (cubic), □ Cd, and ▲ ITO.

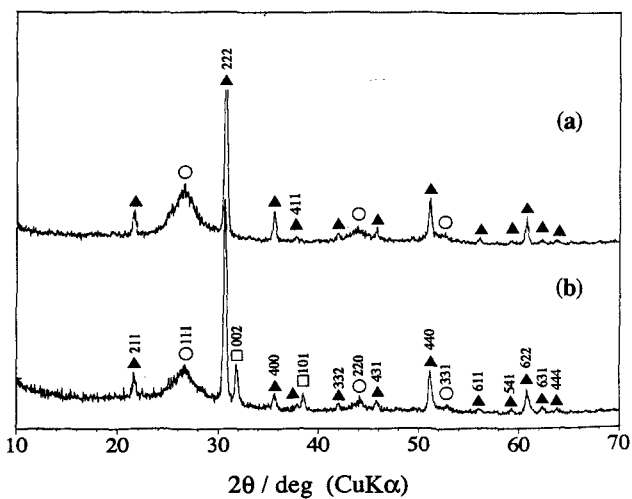


Fig. 3 Effect of Na₂S₂O₃ concentration: (a) 0.050, and (b) 0.0025 mol dm⁻³. ○ CdS (cubic), □ Cd, and ▲ ITO.

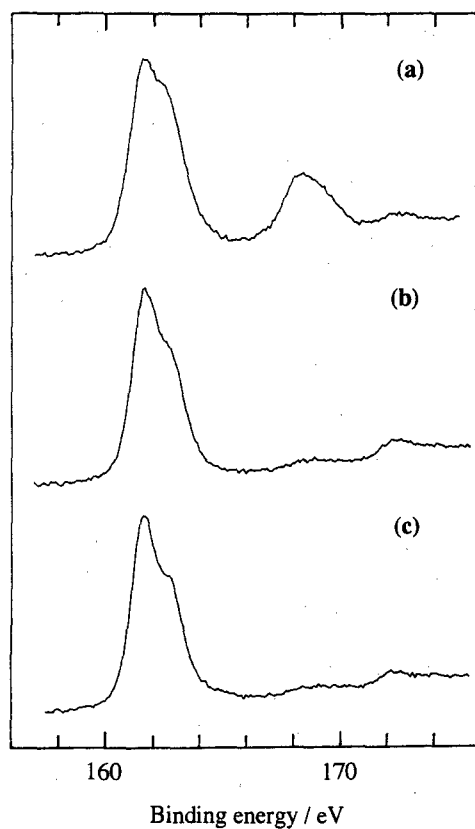


Fig. 4 XPS spectra of S 2p electrons for (a) as-formed film, (b) after heating at 600°C for 5 min, and (c) after heating at 600°C for 10 min.

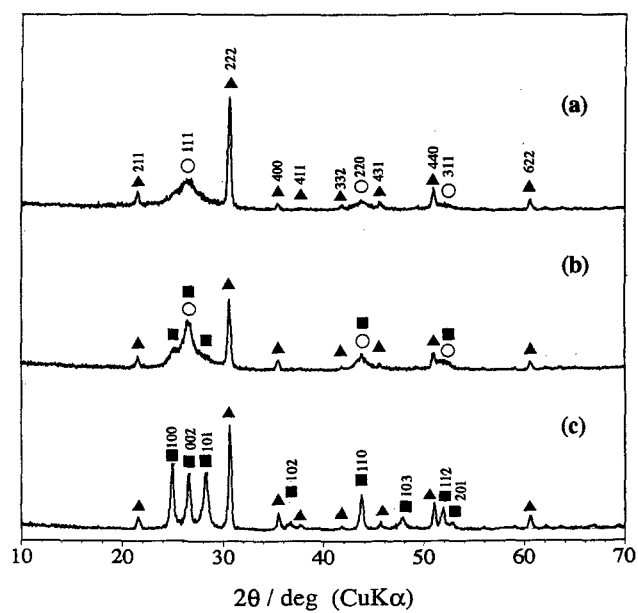


Fig. 5 Structural change by vacuum annealing: (a) as-formed film, (b) after heating at 600°C for 5 min, and (c) after heating at 600°C for 10 min. ○ CdS (cubic), ■ CdS (hexagonal), □ Cd, and ▲ ITO.

electrons for the film formed at -0.82 V composed of two peaks as shown in Fig. 4 (a). The peak at lower binding energy is undoubtedly assigned to sulfide [5,6] from CdS, and that at higher binding energy is due to sulfate [5,6] and/or polythionate ions. Intensity of C 1s peak was comparable to that of S 2p peak, so that adsorbed SDS may not be a major source of the latter peak. It is more likely that sulfate ions and polythionate ions formed by hydrolysis of thiosulfate ions are chemically adsorbed, since the higher binding energy peak cannot be removed completely by ultrasonic rinsing in water or organic solvents such as acetone, alcohol, cyclohexane, and benzene. These indicate that the film is CdS by XRD but the surface is slightly contaminated.

3.3 Annealing of CdS film

To remove surface contamination, vacuum annealing was attempted. The higher binding energy peak in S 2p spectrum disappeared by 5 min heating at 600°C (Fig. 4 (b) and (c)). By this heating, however, crystalline structure started to change, as shown in Fig. 5 (b), and by 10 min heating it became completely wurtzite type (hexagonal structure), as shown in Fig. 5 (c). Auger parameters of Cd for 5 and 10 min heated specimens were 786.3 and 786.5 eV, indicating that the surface became CdS as well as the bulk.

Electric conduction of the 10 min heated film by probe test increased by about ten times compared with the as-formed, though conductivity was not obtained because the film was formed on the conductive ITO glass.

4. Concluding remarks

As above, the present cathodic deposition method from the colloidal sulfur solutions can form compact and adhesive CdS films having thickness of about $1\ \mu\text{m}$. Deposition rate of the film is larger than chemical bath deposition methods [7], considering the quality of film and difference in Cd(II) ion concentration in the solution. Further studies, however, are necessary to attain higher formation rate and to avoid the surface contamination. It may be essential to search more effective surfactants or stabilizing agents.

References

1. H. Minoura, T. Kajita, K. Yamaguchi, Y. Takahashi, and D. P. Amalnerkar, *Chem. Lett.*, 339 (1994).
2. M. Takahashi, S. Haegawa, S. Furuta, and T. Hashino, *Abst. 63rd Ann. Meeting Electrochem. Soc. Jpn.*, p.27 (1996).
3. e. g. B. Jirgensons, and M. E. Straumanis, *A short textbook of colloid chemistry*, Pergamon Press, London (1962).
4. *Kagaku-Benran (Handbook of Chemistry)*, Chemical Society of Japan, p.I-571, Maruzen Co. Ltd., Tokyo (1984).
5. C. D. Wagner, *Practical surface analysis (2nd ed.)*, Ed. by D. Briggs and M. P. Seah, p.614, John Wiley, New York (1990).
6. H. Konno, K. Sasaki, M. Tsunekawa, T. Takamori, and R. Furuichi, *Bunseki Kagaku*, **40**, 609 (1991).
7. e. g. I. Kaur, D. K. Pandya, and K. L. Chopra, *J. Electrochem. Soc.*, **127**, 943 (1980).

Received June 11, 1997

Accepted June 25, 1997