

— Communication —

Effect of Cadmium Precursor Solutions on Fabrication of CdS Thin Films by Successive Ionic Layer Adsorption and Reaction (SILAR) Technique

Mariko SASAGAWA, Junichi NISHINO, and Yoshio NOSAKA*

Nagaoka University of Technology (Kamitomioka, Nagaoka 940-2188, Japan)

Received June 16, 1999 ; Accepted September 1, 1999

CdS thin films were fabricated on ITO-covered glass by successive ionic layer adsorption and reaction (SILAR) technique. The thickness of the CdS thin films increased with increasing the number of SILAR cycles. However, it was about 1/3 of the thickness expected from the ideal deposition process. The surface roughness increased as growth of CdS thin films. To increase the film thickness and to reduce the film roughness, we tried to change counter ions of cadmium ion source solution and to add chelating agent to the solution. In case of using CdCl_2 and triethanolamine, the film thickness was increased and the surface roughness was reduced.

Key Words : SILAR, CdS Thin Films, Chelating Agent, Electroless Solution Deposition

1 Introduction

Successive ionic layer adsorption and reaction (SILAR) technique originated with Nicolau¹⁾ and has been recently studied by Lindroos and coworkers.²⁾ This technique of electroless deposition of thin films is based on the alternative immersion of a substrate into two kinds of precursor solutions to deposit compound semiconductor. Difficulties in the SILAR method are reported to originate from that only 1/3 of the surface is covered with adsorbed ions because of ionic adsorption equilibrium. Then, the surface roughness increases with the film thickness. In the present study, we have aimed at atom-by-atom deposition and tried fabricating CdS thin films by the SILAR technique to investigate the availability of this method. To increase the thickness and to reduce the surface roughness, we changed the cadmium ion source and added some chelating agents to precursor solutions.

2 Experimental

ITO-covered glass was used as a substrate. The substrate was washed in acetone and diluted ethanol (50 % water) with ultrasonic bath, and then electrolyzed in solution³⁾ containing 5 mmol dm^{-3} CdSO_4 , 1 mmol dm^{-3} KOH, and 2 mmol dm^{-3} CH_3COOH to improve the wetness of the substrate surface.

For fabricating CdS thin films, the substrate was alternately immersed into sulfide and cadmium ion solutions for 40 s. Between the immersions, it was rinsed for 40 s by running pure water which was distilled, deionized and then deoxygenated. These steps are defined as one SILAR cycle. In all steps, the substrate was vibrated horizontally to introduce source material ions to the surface of the substrate, and to remove excess adsorbed ions completely. For all the present experiments, concentrations of Cd and

S ions were 20 mmol dm^{-3} and 10 mmol dm^{-3} , respectively. The concentration of chelating agents in Cd ion solution was 20 mmol dm^{-3} . Distilled water purified with Milli-Q was used for preparing all source solutions. Pre-treatment of substrates and deposition of CdS thin films were carried out under a nitrogen atmosphere at ambient temperature.

The number of SILAR cycles was usually 200. For investigating the growth of film thickness and crystallite size, SILAR cycles of 200, 400, 700, and 1000 were employed.

Film thickness was measured by UV-VIS spectroscopy. XRD (X-ray diffraction) was used to elucidate the crystal structure and the crystallite size of films was calculated from the (002) diffraction peak using Scherrer's equation. The elemental analysis was carried out with AES (Auger electron spectroscopy) and XPS (X-ray photoelectron spectroscopy) to check the stoichiometry of the obtained films. Surface roughness was measured with AFM (Atomic force microscopy) as an RMS height in the image of 2 $\mu\text{m} \times 2 \mu\text{m}$ area.

3 Results and Discussion

Figure 1 shows the film thickness and the crystallite size of CdS films as a function of the number of SILAR cycles. The crystallite size was linearly increased with cycles. Comparing to the crystallite size, the film thickness showed rather large value. Above 700 cycles, although the film was still transparent, the surface roughness became large.

Figure 2 shows XRD pattern of the CdS thin film fabricated by 700 SILAR cycles. In case of that CdS films were well crystallized, the films clearly ordered c-axis normal to the surface of the substrate. The peak of (101) diffraction did not appear in the deposi-

tion with a smaller number of SILAR cycles.

Surface morphology was rather rough for the films prepared in the absence of chelating agents. The roughness decreased by adding the agents as indicated in Table 1. Among the agents tested, triethanolamine (TEA) was the most effective to increase the thickness and to reduce the roughness. Surface roughness of the obtained CdS films depends strongly on that of the substrate. Since the substrates used in the present experiments were rather rough, a smoother substrate should be used to elucidate the roughness correctly.

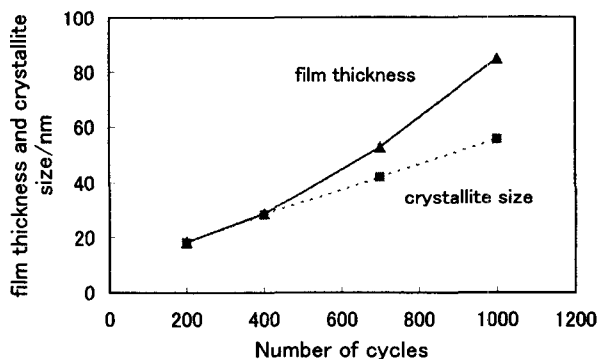


Fig. 1 Thickness and crystallite size of CdS films fabricated by SILAR method as a function of the number of dipping cycles.

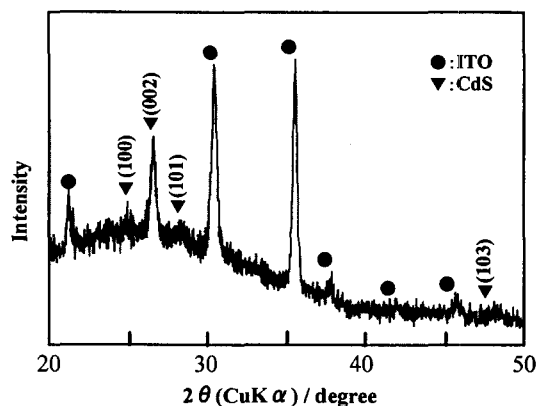


Fig. 2 X-ray diffraction pattern of CdS film fabricated by 700 SILAR cycles in the aqueous solutions of 0.02 mol dm^{-3} CdCl_2 and 0.01 mol dm^{-3} Na_2S .

Table 1 Effect of chelating agent.

Chelating Agent	Film thickness	Crystallite size	Surface roughness ^{a)}
None	18 nm	23 nm	5.3 nm
2-mercaptoethylamine hydrochloride	46	–	8.9
Ethylenediamine	19	–	6.0
Triethanolamine	25	24	4.1
Monoethanolamine	17	–	4.0
Nitrirotriactic acid trisodium salt	21	–	3.5

a) Roughness of the substrate was 4.1 nm.

AES spectra were shown in Fig. 3. Where (a) was obtained for single crystal CdS, (b) was for a CdS thin film fabricated without TEA, and (c) was with TEA. Only the peaks of Cd and S were detected. We also carried out XPS measurements to detect impurities and confirm the stoichiometry of the CdS films. As a result, possible contamination of carbon was not detected in both AES and XPS measurements for these films. These experimental evidences showed the fact that the films obtained with TEA are almost stoichiometric.

We tried film formation by changing cadmium source as listed in Table 2. When $\text{Cd}(\text{CH}_3\text{COO})_2$ was used, the film was well crystallized. The film thickness, however, was not increased and the surface roughness was larger than the film thickness. When CdCl_2 was used, the obtained film was thicker, with a larger crystallite size and a smaller surface roughness.

To obtain a better film, the chelating agent TEA was coupled with various cadmium ion sources. Transparent CdS films were, however, obtained only in case of using CdCl_2 and CdI_2 . The surface roughness for CdI_2 , similarly to CdCl_2 , was reduced in the presence of TEA.

It was found that, in case of using CdCl_2 as a

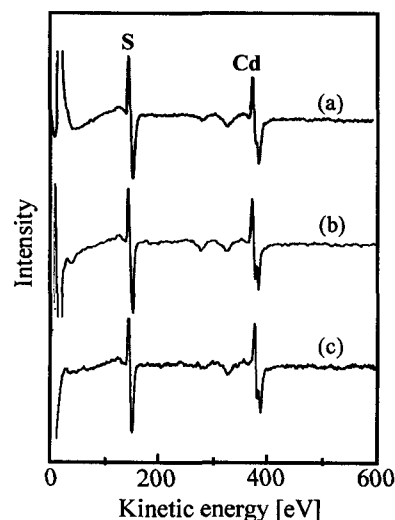


Fig. 3 Auger electron spectra of (a) single crystal CdS, CdS thin Films Fabricated by SILAR technique (b) without and (c) with triethanolamine. Both (b) and (c) were obtained with 200 SILAR cycles.

Table 2 Effect of counter ions of Cd^{2+} .

Cadmium ion source	Film thickness	Crystallite size	Surface roughness ^{a)}
Cadmium chloride	18 nm	23 nm	5.3 nm
Cadmium fluoride	24	20	17.2
Cadmium iodide	27	–	26.3
Cadmium perchlorate	13	–	4.8
Cadmium acetate	20	26	11.0

a) Roughness of the substrate was 4.1 nm.

cadmium source, we could obtain the best quality film comparing with those from other halide salts. Since Cl^- has the same atomic radius to S^{2-} , the size may affect the ionic adsorption and reaction in SILAR cycles. Among the chelating agents tried, TEA gave CdS films of which characteristics are close to those we expected.

In conclusion, by adding chelating agents, we could increase the film thickness and reduce the surface roughness. We are now studying to improve further the property of the films by selecting the optimum substrate materials and precursor solution.

Acknowledgment

The present work is partly defrayed by a Grant-in-Aid for Scientific Research (No.09237105) on Priority-Area-Research of "Electrochemistry of Ordered Interfaces" from the Japanese Ministry of Science, Education and Culture.

References

- 1) Y. F. Nicolau, *Appl. Surf. Sci.*, **22/23**, 1061 (1985).
- 2) M. P. Valkonen, S. Lindroos, R. Resch, M. Leskelä, G. Friedbacher, and M. Grasserbauer, *Appl. Surf. Sci.*, **136**, 131 (1998).
- 3) U. Demir and C. Shannon, *Langmuir*, **10**, 2794 (1994).