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Electrochemical evaluation of the roles of chelating reagents in Cd ion adsorption on CdS surface for the successive ionic layer adsorption and reaction (SILAR) deposition

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Abstract

We evaluated the effect of the chelating reagents in the SILAR (successive ionic layer adsorption and reaction) process by monitoring the formation of one layer of CdS on S surface of the CdS layers prepared by successive UPD (under potential deposition) method. Anodic stripping voltammetry was adopted to measure the amount of CdS deposited on Au substrate. Among the chelating reagents examined, the order of the ability to enhance the deposition by dipping was cysteine > (None) > mercaptoethylamine > triethanolamine >> ethylenediamine. Considering the stability constant of the chelating reagents to Cd ions, the present experimental result showed that tight binding of Cd atoms to the surface S atoms is an important step in the deposition of CdS by SILAR method.

Keywords : CdS; ligand; deposition; stripping voltammetry

1. Introduction

A pair of ions having an extremely low solubility product is probably adsorbed tightly on a solid surface of corresponding reverse ions. Based on this concept, it is expected that thin film could be fabricated by alternate adsorption of such ions. This principle leads one of the liquid phase methods for fabricating compound semiconductor thin films, which is called the successive ionic layer adsorption and reaction (SILAR) method [1]. For example, in case of the fabrication of CdS thin films by the SILAR method, a substrate is dipped (DIP) alternately into each solution containing Cd or S ions [2,3]. Our previous study of the deposition on ITO coated glass showed that the thickness of the CdS thin film was increased linearly with the number of DIP in the SILAR process. The present authors have carried out the experiments

that were focused on the search for an optimal solution condition to increase the film thickness. As for Cd ion solution, six Cd salts and six chelating reagents were tried for the counter ion and the ligand, respectively. The optimal reagents were selected by evaluating the film thickness of the 200 layers of CdS [4]. As a result, we found that Cl⁻ was suitable for the counter ions, and that triethanolamine and cysteine were useful for the chelating reagent. In the previous study, however, no information about the reaction at each deposition step has been obtained since the thickness was merely measured for the films deposited by 200 layers. Furthermore, the preparation of the sample was of time consuming.

To evaluate the reaction of atomic layer deposition, it is convenient if the amount of Cd ions adsorbed at the S surface of CdS can be measured. Stripping voltammetry may be applicable to evaluate the amount of the deposition. In the present study, we utilized S surface of CdS prepared by UPD (under potential deposition) method. Namely, one and a half layers of CdS (Au/S/Cd/S) were fabricated at first on an Au substrate and then one layer of CdS was formed by successive dipping into the solutions containing chelated Cd and S ions.

The two and a half layers of CdS thin film (Au/S/Cd/S/Cd/S) thus obtained was measured for the amount of charges on oxidative desorption. Then the effect of chelating reagents on the adsorption of Cd ion was explored in connection with the thin film fabrication by the SILAR method. The result was comparable with that of the previous SILAR experiment, and then this methodology appeared to be useful to investigate the effect of the chelating reagent on the atomic layer deposition.

2. Experimental

As the working electrode in the present study, a cross section of polycrystalline Au wire of 1mm in diameter was used. This electrode was polished to obtain a mirror-like surface followed by rinsing it ultrasonically in ultrapure water. Then it was electrolyzed in 1M H₂SO₄ solution deoxygenated by N₂ gas flow until typical current-voltage (CV) curve of Au electrode was observed [5]. In this treatment, the potential ranged from -100 to 1600 mV vs. Ag/AgCl and the sweep rate was 100 mVs⁻¹. An Ag/AgCl (3M NaCl) electrode (BAS, Co., RE-1B) and a coil of Pt wire of 1mm in diameter were used as the reference and counter electrodes, respectively.

Aqueous solution of 0.02 M CdSO₄ was used as Cd ion source for both the DIP and UPD processes. The same chelating reagents as our previous SILAR experiment, cysteine (Cys), mercaptoethylamine (MEA), triethanolamine (TEOA), and ethylenediamine (EN), were employed in the present study. Among these four chelating

reagents, Cys and MEA contain thiol group and the all reagents are kinds of amines. The concentration of the chelating reagent added to Cd solution was 0.02 M. Even though the pH of the Cd solution changed by adding the reagent, it was not adjusted since the desired ionic adsorption may be interfered by the addition of extra ions [6]. As for S ion solution, 0.01 M Na₂S was used. The concentrations of these solutions were identical to those in the previous SILAR experiment for 200 CdS layers.

The electrolytes used for UPD processes of S and Cd were 0.1 M Na₂SO₄ (pH=4.82) and 0.1 M CH₃COONa (pH=8.10), respectively [7]. The water purified with Milli-Q system was used for preparing all solutions and rinsing the electrodes. The amount of the solutions of Cd and S was 50 ml for each and all of the solutions were deoxygenated by N₂ bubbling.

Figure 1 illustrates the processes of the thin film formation in the present study. After Au/S/Cd/S layer was formed by successive UPD for the common substrate, cadmium ions combined with ligand (Cd-L) are adsorbed on the S surface layer in DIP-1 process (a) and then L in Cd-L layer are replaced by S ions in DIP-2 process (b). The deposition is finished by the S adsorption since the adsorbed Cd layer is hopefully stabilized by replacing L for S [7]. Therefore, the CdS films of totally two and a half layers consists of the one and a half UPD-CdS layers and the one DIP-CdS layer.

In order to reduce the possible effect of the Au substrate on the surface adsorption, two and a half UPD-CdS layers were tried to use as a common substrate in place of the one and a half UPD-CdS layers. In this case, however, variation among the amounts of the charge observed in the anodic desorption was too small to evaluate the difference. Then the one and a half UPD-CdS layers were used as the base in the present study.

The amount of deposited CdS was evaluated from the charge for anodic desorption of the thin films in a 1M H₂SO₄ solution deoxygenated by N₂ bubbling where the potential was swept from -100 to +1600 mV (vs. Ag/AgCl) at the rate of 100 mVs⁻¹. The amount of deposited CdS was evaluated by subtracting the amount of charges obtained for the clean Au electrode [5]. The measurements of desorption charges were carried out for four samples of each solution, and the averaged value was shown in the plot.

3. Results and discussion

Figure 2 shows some typical voltammograms for anodic desorption of the CdS thin films, in which the single surface layer was prepared in the absence of chelating reagent, (None) (a), in the presence of Cys (b) and TEOA (c). Where Cys and TEOA represent thiols and amines, respectively. In the presence of the chelating reagent, the

potential of the first wave shifted to the lower side and that of the second wave became higher when they are compared to the case of None. For the other chelating reagents, similar tendencies were observed. This observation may be explained by that the current originates from the oxidation of chelating reagent remained possibly in the CdS layers. No chelating reagent, however, is probably contained in the CdS film. Actually, the absence of the chelating reagents was proved by detecting no carbon atoms in the AES measurement for a CdS thin film deposited by the SILAR method in our previous study. Therefore, the measured currents originated from only oxidative desorption of CdS. Then the observed potential shift implies that the state of CdS prepared with chelating reagents was different from that deposited without chelates.

Figure 3 shows the desorption charges for various chelating reagents, which are calculated by integrating the anodic current represented in Fig.2. For comparison, the result obtained for the sample prepared by adding one UPD-CdS layer, or totally two and a half UPD layers, was shown as (f). The broken line shows the amount of charge corresponding to the decomposition of the common CdS of one and a half UPD layers. Therefore, the comparison in the amounts of charge above the broken line should be used to evaluate the effect of the chelating reagents on the adsorption of uppermost CdS layer formed by DIP process. As shown in Fig.3, even when the uppermost layer was formed by DIP ((a)-(e)), the amount of charges is comparable to that of the two and a half UPD-CdS layers (f). In the case of Cys among the four chelating reagents, almost same stripping charge was observed. This experimental result indicates that the atomic level deposition of CdS can be achieved based on the ionic adsorption by DIP similarly to the case of electrochemical adsorption by UPD. The order of ability to enhance the deposition of CdS was Cys > (None) > MEA > TEOA >> EN. In our previous SILAR experiment, where the samples were prepared by the deposition of 200 CdS layers, the order of the enhancement was MEA > Cys >> TEOA >> EN (>None). Then, the result of the present study showed almost the same tendency in the order to that in the previous study. Thus the reagents having SH group was confirmed to be useful to increase the film thickness. Especially, Cys provided the best film among the reagents tested. Since the measurement for one layer of adsorbed CdS was achieved as mentioned above, the stripping voltammetry appeared to be applicable to an atomic level evaluation for the amount of CdS thin film.

In the present study, two DIP processes are included in the deposition of one CdS layer as illustrated in Fig.1. The first step works to adsorb Cd-L to the surface S of the one and a half UPD-CdS layers and the second step devotes to substitute the L of adsorbed Cd-L for S. Then which step does affect the difference in the amount of

deposition? In terms of the stability constant for Cd^{2+} and L in bulk solution, it seems harder to substitute S ions for ligands having a larger stability constant. The amount of CdS deposited with EN was lower than that with TEOA as observed in the case of SILAR experiment. Since the stability constants, $\log \beta_1$, were 3.15 and 5.69 for TEOA and EN, respectively[8], the high stability may prevent the second step. However, the strength of coordination of these amines is weaker than that of thiols, e.g., $\log \beta_1$ of Cys is 12.88[9]. Then, it may conclude that the easy desorption of the ligands in the second step causes no effect on the efficiency of the deposition. Since TEOA is a kind of sacrificial electron donor similarly to thiols, its donating character may give an advantage to the Cd ion adsorption in the first step of DIP method. Therefore, the present observation suggests that the formation of a strong combination of Cd to S surface at the first step is more important than the substitution of L for S at the second step for the deposition of CdS by SILAR method.

In conclusion, the amount of one layer of CdS deposited by SILAR with Cd-L on the surface of the one and a half CdS layers formed by UPD was successfully evaluated by anodic stripping voltammetry. It was confirmed that CdS could be deposited by alternative dipping in SILAR method similarly to the electrochemical UPD method. Especially, in case of using the chelating reagents having SH group, the amount of CdS deposited was almost equal to that obtained by UPD. Furthermore, we could conclude that, to improve the deposition of CdS thin film by SILAR method, the adsorption of Cd ions on CdS surface is more important rather than the adsorption of S.

References

- [1] Y.F. Nicolau, *Appl. Surf. Sci.*, 22 (1985) 1061.
- [2] M.P. Valkonen, Tapio Kanninen, Seppo Lindroos, Markku Leskelä and Eero Rauhala, *Applied Surface Science*, 115 (1997) 386.
- [3] C.D. Lokhande, B.R. Sankapal, H.M. Pathan, M. Muller, M. Giersing and H. Tributsch, *Applied Surface Science*, 181 (2001) 277.
- [4] M. Sasagawa and Y. Nosaka, *Phys. Chem. Chem. Phys.*, 3 (2001) 3371.
- [5] L.P. Colletti, D. Teklay and J.L. Stickney, *J. Electroanal. Chem.*, 369 (1994) 145.
- [6] Y.F. Nicolau and J.C. Menard, *J. Colloid and Interf. Sci.*, 148 (1992) 551.
- [7] T. Torimoto, S. Nagakubo, M. Nishizawa and H. Yoneyama, *Langmuir*, 14 (1998) 7077.
- [8] D.D. Perrin, *Stability Constants of Metal-Ion Complexes, Part B: Organic Ligands*, Pergamon Press, Oxford, 1979.
- [9] M.D. Walker and D.R. Williams, *J. Chem. Soc., Dalton Trans.* (1974) 1186 ; E.

Bottari and M.R. Festa, *Talanta*, 44 (1997) 1705.

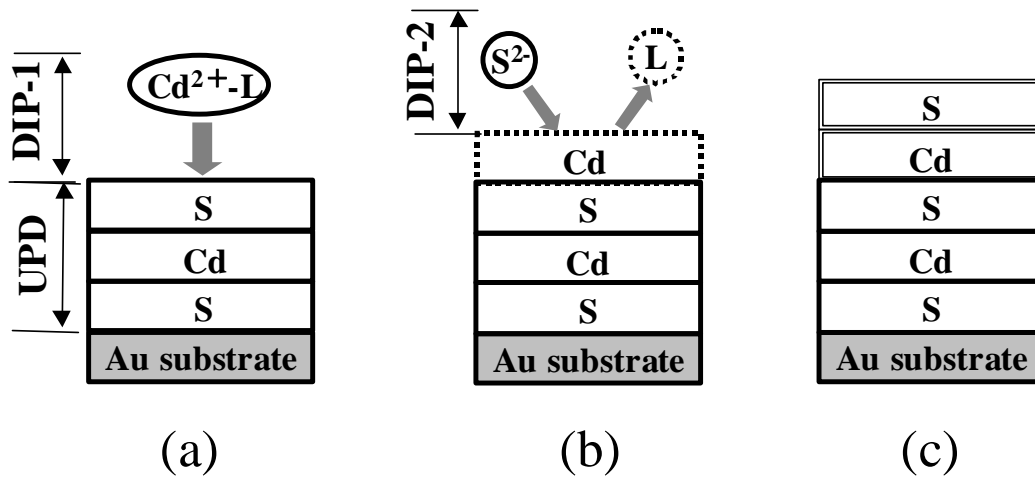


Fig. 1. Schematic illustrations for the dipping (DIP) processes of CdS layers in the present study. (a) Adsorption of Cd^{2+} with ligand L on UPD-prepared S/Cd/S layer in DIP-1 process. (b) Replacement of L by S^{2-} in DIP-2 process forming one CdS layer as shown by (c).

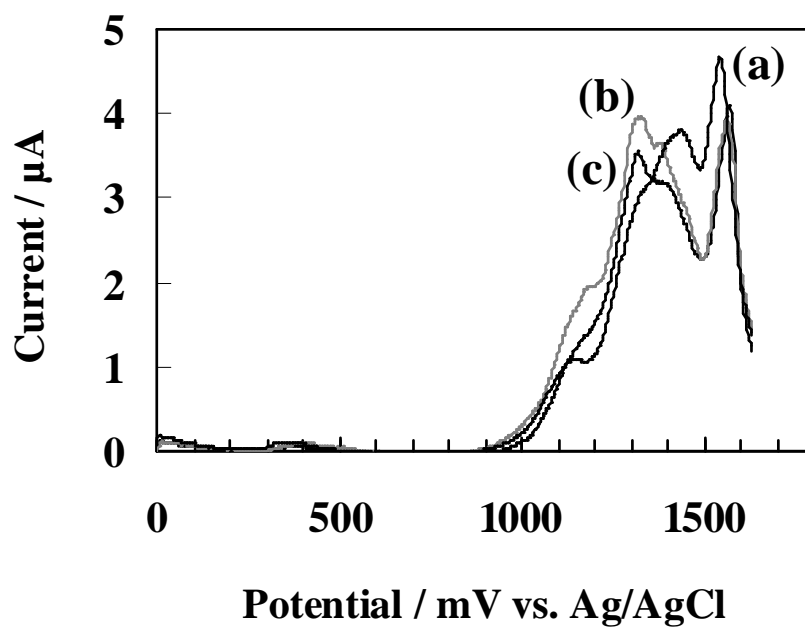


Fig. 2. Anodic stripping voltammograms for the two and a half CdS layers deposited by the processes shown in Fig. 1. CdS layer was obtained without chelating reagent (a), with Cys(b) and TEOA(c) as a chelating reagent, respectively.

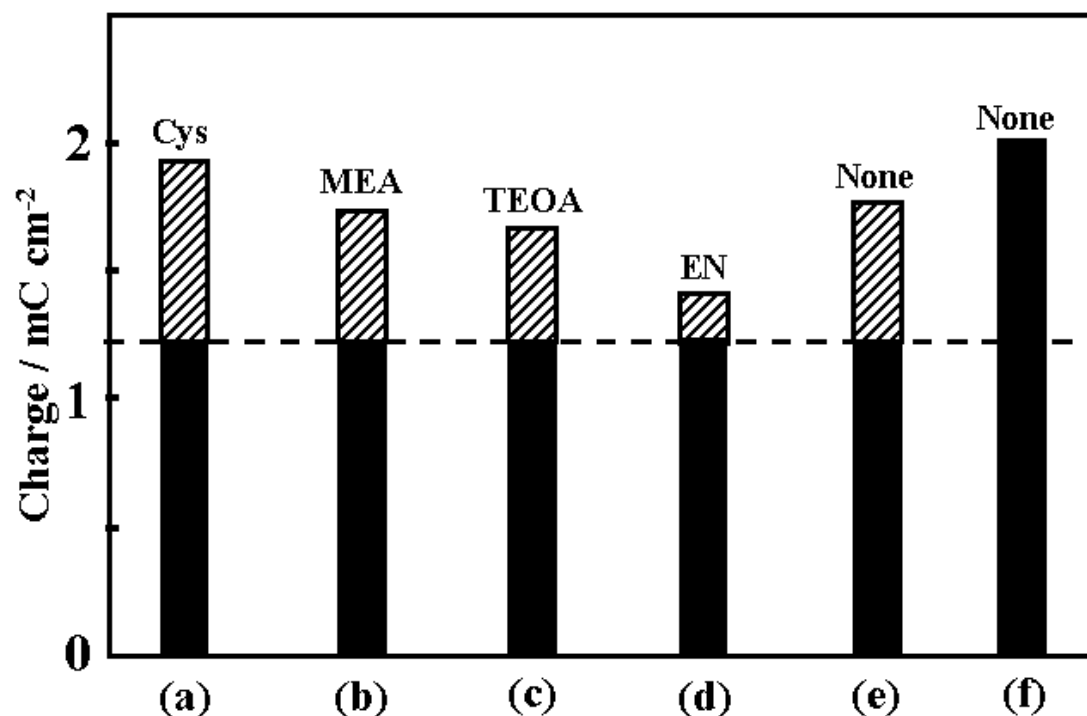


Fig. 3. Amount of charges through stripping of CdS layers, which are deposited by UPD for the first one and a half layers followed by dipping (DIP) for the last one layer where Cd solution contains each ligand, cysteine (a), mercaptoethylamine (b), triethanolamine (c), ethylenediamine (d). The broken line indicates the amount of charges required to strip one and a half UPD layers. For comparison, (f) is the sample that the additional one layer was also prepared by UPD. Dark area (■) and hatched area (▨) show UPD and DIP processes, respectively.