

Studies on the effects of Cd ion sources and chelating reagents on atomic layer CdS deposition by successive ionic layer adsorption and reaction (SILAR) method

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CdS thin films were fabricated on an ITO-covered glass substrate by successive ionic layer adsorption and reaction (SILAR) method under various conditions. By changing Cd ion sources, chelating reagents, and pH, the obtained films were evaluated by their thickness, crystallinity, crystallite size, surface roughness, and elemental composition. CdCl₂ and triethanolamine were found to provide the most well crystallized thick film among six Cd salts and six chelating reagents. In the present study, no marked effect of pH on the film quality was observed compared to the effect of the difference in the counter ions. The effects of counter ions, chelating reagents, and pH could be explained by the discussion in terms of the stability constant of Cd²⁺ for these chemical species and SH⁻.

1 Introduction

Semiconductor thin films are fabricated by several methods both in gas and liquid phases. By comparing to gas phase methods, liquid phase methods have an advantage of providing thin films of large area at low costs but a disadvantage of difficulty in the control of a precise film structure. In fabricating semiconductor thin films, it is desired to control the structure of the films at an atomic level. Particularly, the control of surface flatness is required for many applications such as solar cells.

Recently, electrochemical atomic layer epitaxy (ECALE) method developed by Stickney¹⁻⁴ is widely exploited for the fabrication of compound semiconductor thin films. This method achieved the control of the film structure at an atomic level by using UPD (under potential deposition) procedure. On the application of this technique to semiconductor materials, however, considerable conductivity is required for the obtained films. Namely, the process of the electrodeposition requires the transformation of carriers from the electrode to the surface of the deposited film. Therefore, there seems to be an intrinsic limitation in the thickness of the films whose structure is controllable with the applied potential. To overcome the problem of the conductivity, we employed an electroless deposition method named the successive ionic layer adsorption and reaction (SILAR) method,⁵⁻⁸ which was initiated by Nicolau in 1985 and developed by Lindroos *et al.*⁹⁻¹¹ and Lokhande *et al.*¹²⁻¹⁴ In this method thin films are fabricated by alternative dipping into two solutions of each precursor ion for compound semiconductors. Therefore, the control of the film thickness becomes feasible by

changing the number of the dipping cycles. Furthermore, atomically controlled multilayer thin films or super lattice can be possibly fabricated by changing precursor solutions. Since the SILAR method depends only on the immersing the substrate into the solutions, the deposition of films with large area can be achieved at low costs. Recently, this method was used for the fabrication of ZnS semiconductor thin films from aqueous solutions at laboratory level as well as the CBD (chemical bath deposition) method.^{15,16} Although several studies on this method have been carried out, no systematic research for the effect of precursor solutions have been reported in literature so far.

On the other hand, the SILAR method has a few disadvantages. Since the adsorption of ions at the film surface precedes the atomic deposition, the surface should be covered by precursor ions completely at each SILAR step. Consequently, for fabricating structure-controlled thin films by the SILAR method, it is essential to select the precursor solutions so as to completely adsorb the ions at the surface. The information about the factors that control the ion adsorption equilibrium at the solid-liquid interface would provide a clue to develop the technique to fabricate thin films of compound semiconductors. This key factors become important not only for the SILAR method, but also for the other liquid phase deposition methods such as the CBD method.

In the present study we investigated the various Cd ion sources and chelating reagents as factors affecting the properties of CdS film such as film thickness, crystallinity, crystallite size, surface roughness and elemental composition. Six Cd sources were employed in the present study. Among them,

CdF₂, CdCl₂, and CdI₂ were used to investigate the effect of halide ions, while Cd(CH₃COO)₂ and Cd(HCOO)₂ were used to know the effect of organic counter ions. And Cd(ClO₄)₂ was tried because the adsorption of ClO₄⁻ ions to solid surface is less specific than that of Cl⁻ ions. As for chelating reagents, 2-mercaptoethylamine (MEA) and cysteine (Cys) were used because we found that these thiols are adsorbed on CdS surface and control the growth of CdS particle in the previous study.¹⁷ Besides the thiols, amines such as ethylenediamine (EN), triethanolamine (TEOA), and monoethanolamine (MEOA) were also employed as chelating reagents.

pH of the precursor solutions may be one of the important parameters for the fabrication of semiconductor thin films in aqueous system, because the difference of pH presumes the dissociation state of several ions and the formation of Cd(OH)₂ that often prevents the formation of CdS thin films in solutions. Therefore, we examined also the effect of the pH on the material properties of CdS films by the SILAR method and discussed the factors necessary for the fabrication of qualified thin films.

2 Experimental

2.1 Substrate

Indium tin oxide (ITO) coated glass plate (Nippon Seiki) was cut by 7 mm × 50 mm and washed ultrasonically in acetone and then in 50% ethanol water for each 10 minutes.¹⁸ As a pretreatment, the substrate was electrolyzed for 30 minutes in a deoxygenated aqueous solution containing 5 mM CdSO₄, 1 mM

KOH, and 2 mM CH₃COOH.¹⁹ The electrolytic potential was swept cyclically between +450 and -500 mV by an HA-301 potentiostat (Hokuto Denko) with an Ag/AgCl reference electrode (BAS Co. Ltd.) and a Pt wire counter electrode. By treating the ITO glass substrate electrochemically, we could obtain hydrophilic surface and uniform CdS deposition resulted without growth of undesired particles.

2.2 Solutions

Six Cd salts, that is, CdF₂, Cd(ClO₄)₂ (Soekawa Chemicals Co.), CdCl₂, CdI₂, Cd(CH₃COO)₂ and Cd(HCOO)₂ (Nacalai Tesque Co.), were employed as Cd ion sources on 0.02 M aqueous solutions. 2-Mercaptoethylamine hydrochloride (MEA), cysteine (Cys), ethylenediamine (EN), triethanolamine (TEOA), monoethanolamine (MEOA), and nitrilotriacetic acid trisodium salt (NTA) were purchased from Tokyo Kasei Inc. Co. and used as the chelating reagents. The concentration of the chelating reagents in Cd ion solution was 0.02 M. In some cases pH of Cd ion solution was adjusted with HCl and NaOH to avoid the precipitation of Cd(OH)₂ in the preparation procedure. Freshly prepared 0.01 M Na₂S aqueous solution was used as S ion source. Water was distilled and treated by a Milli-Q system. All of the reagents were used as received without further purification.

2.3 Deposition method

Figure 1 shows the diagram of the system used in the present study for

SILAR deposition. Both pretreatments and SILAR dipping of the substrate were carried out in a glove box, where the concentration of oxygen was reduced to be less than 0.1 % by purging N₂ gas because it is reported that oxygen prevents the formation of CdS in SILAR method.⁸ Water for rinsing the substrate was also deoxygenated by N₂ bubbling. The deposition was performed at room temperature and under ambient pressure.

A pretreated ITO glass substrate was immersed into 50 ml of S solution in a 100 ml beaker with a magnetic stirrer for 40 s followed by rinsing for 20 s with a water flow at the rate of 6 ml/s. Then, it was immersed into a stirred Cd solution for 40 s followed by rinsing with the water flow for 20 s. When the substrate was immersed in solutions, it was vibrated to accelerate the diffusion of solute. The 4 steps of different dipping are regarded as one SILAR cycle, and the CdS thin film grew on the substrate by repeating these steps. The number of SILAR cycles was fixed to 200 except when the effect of the number of cycles up to 1000 was investigated on the thickness and the crystallite size.

2.4 Evaluation methods

The quality of the obtained film was evaluated by measuring thickness, crystallinity, crystallite size, surface roughness, and elemental composition. The film thickness was calculated from the difference of absorbances at wavelengths of 350 and 600 nm, which were measured by a U-3210 UV-vis spectrophotometer (Hitachi). The crystallinity and the crystallite size were measured by X-ray diffraction (XRD) with an M03HF22 diffractometer (Material Analysis and

Characterization Science) using $\text{CuK}\alpha$ radiation. The surface roughness was measured as Ra value with an SPI-3700 atomic force microscope (AFM) equipped with an SPA-300 probe head (Seiko Instruments). The Ra values were calculated at three scan areas of $2\ \mu\text{m} \times 2\ \mu\text{m}$ and used them as averaged one. The elemental composition was measured by Auger electron spectroscopy (AES) with a JAMP-10SX spectrometer (JEOL Inc.), and X-ray photoelectron spectroscopy (XPS) with a JPS-100SX spectrometer (JEOL Inc.). Argon etching was performed to clean the film surface by eliminating the adsorbed carbon, and to obtain the depth profile. The pH of the solutions was measured immediately after the preparation of the solutions.

3 Results and Discussion

3.1 The film thickness and the crystallite size.

Figure 2 shows the XRD patterns of the thin films obtained by SILAR method of 200 to 1000 cycles using CdCl_2 and Na_2S solutions. The peak at $2\theta = 26.5^\circ$ can be assigned to both the diffraction of cubic (111) and hexagonal (002) plane of CdS crystal because the reported values of 2θ are 26.506° ²⁰ and 26.507° ²¹, respectively. Above 700 cycles, the diffraction peaks assigned to hexagonal (100), (101), and (103) were observed. This observation is consistent with the report that hexagonal CdS crystallite on an ITO substrate with a strong {0001} preferred orientation were obtained by the SILAR deposition.⁷ Then the crystal structure of the present CdS films was also assigned to hexagonal. The large grains oriented to hexagonal (002) were reported for the CdS films prepared by

the CBD method with CdCl_2 .²² Furthermore, the XRD peaks of hexagonal (100), (002), and (101) of CdS were also reported for the film with electrodeposition on an ITO glass.²³ These reports in literature support our assignment of the crystal structure.

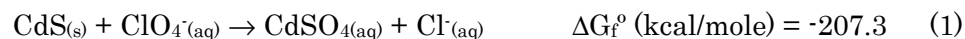
The film thickness and the crystallite size were increased linearly with the number of cycles as shown in the previous brief report,²⁴ indicating that the same deposition reaction occurs at each SILAR cycle. Thus we confirmed that the film thickness can be controlled by changing the number of the cycles. Below 400 cycles, the crystallite size is equal to the film thickness, suggesting that the deposition occurs by mono crystalline formation. Since the distance of (001) planes of hexagonal CdS is 0.3360 nm²¹, this value is expected to be the growth rate by one SILAR cycle. However, the growth rate obtained in the present experimental condition was about 0.1 nm per cycle. Namely, one molecular layer was not obtained by one SILAR cycle. In order to improve the growth rate, the amount of ions adsorbed by each immersion must be increased by shifting the surface adsorption equilibrium to full coverage.

3.2 The effect of the counter ions.

Since counter anions should accompany Cd cations in aqueous solution, first we tried to change the counter anions. Figure 3 shows the thickness, crystallite size, surface roughness, and composition ratio of CdS films obtained for six different counter ions. Since CdS films prepared with CdI_2 and $\text{Cd}(\text{ClO}_4)_2$ provided no XRD peak, the value of crystallite size could not be obtained. In the

case of CdF_2 and $\text{Cd}(\text{CH}_3\text{COO})_2$, the film thickness was relatively large and the crystallinity was high, but the surface was rather rough. On the other hand, CdCl_2 and $\text{Cd}(\text{HCOO})_2$ gave well crystallized CdS films with a small surface roughness though the film thickness was not large as compared with that for CdI_2 and CdF_2 . These results suggest that CdCl_2 and $\text{Cd}(\text{HCOO})_2$ are the most potential Cd ion sources. Especially, $\text{Cd}(\text{HCOO})_2$ gave a flat film with a surface roughness of 4.2 nm which comparable to that of the substrate (4.1 nm). Actually, the surface structure of the CdS film observed by AFM showed the same feature as that of the ITO glass substrate itself. The thickness and crystallite size for the film with $\text{Cd}(\text{HCOO})_2$ were 18.2 nm and 18.6 nm, respectively. In spite of the well crystallized film, the atomic composition of S/Cd was less than 0.8 as shown in Figure 3. On the other hand, the film obtained from CdCl_2 was stoichiometric CdS because the elemental composition ratio was nearly unity.

The solubilities of CdF_2 and CdI_2 are 4.1²⁵ and 46.3,²⁶ respectively. On the other hand, that of CdCl_2 is 121,²⁷ and $\text{Cd}(\text{CH}_3\text{COO})_2$ and $\text{Cd}(\text{HCOO})_2$ are also very soluble. Figure 3 shows that the Cd salts with low solubility in water give thicker films. This observation suggests that Cd ions adsorbed on the surface of the growing film would be stabilized by the coordination of the counter ions and then Cd ions are involved in the crystal lattice more easily. Although the solubility of $\text{Cd}(\text{ClO}_4)_2$, 58.8,²⁶ is lower than that of CdCl_2 , ClO_4^- counter ions did not give a thicker crystalline film than Cl^- as indicated in Figure 3. Since ClO_4^- ion is reported to oxidize CdS as equation (1),⁸ this counter ion may act to release Cd-S bond.



Thus, $\text{Cd}(\text{ClO}_4)_2$ might give less crystallized film. Consequently, CdCl_2 would be the most suitable Cd ion source among the tested Cd salts ; CdF_2 , CdCl_2 , CdI_2 , $\text{Cd}(\text{ClO}_4)_2$, $\text{Cd}(\text{CH}_3\text{COO})_2$, and $\text{Cd}(\text{HCOO})_2$.

In order to explain the effect of counter ions, you should recall that Cd^{2+} and S^{2-} ion must be adsorbed on and react with the surface atoms of the growing crystal in the SILAR method. When CdS grows by Cd atom, Cd ions are adsorbed on the $-\text{SH}$ surface.⁸ The reaction step may be expressed as the substitution of CdL^+ for H^+ .



Where L represents a ligand, which is possible to be OH^- as well as counter ions of Cd salt. On the step where CdS grows by S atoms, SH^- ions are adsorbed to the $\text{Cd}\cdot\text{L}$ surface. This step may be expressed as the substitution of SH^- for L.



That is, when a CdS film grows by one Cd atomic layer, surface H atoms are replaced by Cd atoms bound with L, and when it grows by one S atomic layer, an L bound to the surface Cd atoms is replaced by an SH group. It would be

desirable that the adsorption of L are stabilized and then successively removed by SH⁻. Thus, complete adsorption of ions at the desired surface site and the smooth substitution of these ions are inevitable to obtain highly qualified thin films by the SILAR method.

The above consideration of the reaction step suggests that the properties of the obtained film may be affected by the strength of the coordination bond between surface Cd and L. As a measure of the coordination strength, the stability constant, logK_n, can be employed. Here, K_n represents the equilibrium quotients as equation (4) and (5).



$$K_n = [\text{CdL}_n] / [\text{CdL}_{n-1}][\text{L}] \quad (5)$$

Stability constants logK₁ of Cd²⁺ with the counter ions used in the present study ranges from 0.76 to 2.3,²⁸⁻³² and are listed in Table 1. The value of logK₁ for SH⁻, 7.6, is higher than those of the counter ions. Furthermore, SH group in protein is known to have high affinity to metal ions such as Cd²⁺. The facts mentioned above, support the assumption that CdL⁺ ions in solution can be adsorbed to the surface SH group of CdS film (eq.2) and then the attached ligand can be replaced with SH⁻ (eq.3). Since CdS is very insoluble in water, once Cd-S bond is formed, it is able to remain on a substrate. Thus, stability constant of ligands may apply for discussing the effect at the surface. However, the other factor may present for ligands having similar stability constants. Nicolau *et al.* reported that the

amount of ionic species adsorbed on the surface becomes larger in the order of $\text{HCOO}^- > \text{Cl}^- > \text{SO}_4^{2-}$.⁸ This order is opposite to that of $\log K_1$ for Cd^{2+} ions in solution as shown in Table 1. Then applications of $\log K_1$ to the solid-liquid interface must be careful because $\log K$ is derived for the coordination of metal ions in solutions. However, $\log K$ could be used to discuss the behavior of ions at solid surface as a first approximation.

Figure 3 shows that the crystallite size and the S/Cd ratio of the film obtained with CdCl_2 is larger than that of $\text{Cd}(\text{HCOO})_2$. This result may suggest that the substitution of S for L did not occur easily with this ligand. This is consistent with the order of the amount of the surface adsorption reported by Nicolau. Thus, a strong coordination of L to Cd at the surface loses S atoms in the deposition process because of the difficulty of the substitution, while a weaker coordination loses the stability of surface Cd atoms. Therefore, moderate strength in adsorption of L to Cd is preferred. This respect was realized by the experimental result in which Cl^- ion is a suitable counter ion.

We may be able to take the principle of soft and hard acids and bases (SHAB)^{33,34} into account of the discussion about the ion adsorption on the deposited film. In SHAB concept, soft anions have high affinity for soft cations. Cd^{2+} is classified into soft cations. S^{2-} and I^- are soft anions, while ClO_4^- , Cl^- , and F^- are hard anions. Then, this principle is also applicable to explain the experimental results. That is, a moderate strength in counter anion, i.e. hard bases of anion against the soft acid of Cd^{2+} , is favorable to use as precursor solution for the SILAR method.

The radius of ions may also affect the properties of the films obtained by a SILAR method because a highly packed adsorption arrangement seems essential for a qualified film. Because the ionic radius in solution includes the size of hydration waters, we used the radii derived for crystalline for the present study. The radius of S site was estimated to be 2.07 Å as a half of the lattice constant for hexagonal (002) plane.²¹ This value is slightly larger than the crystallite radius 1.84 Å³⁵ of S²⁻. Since the crystal radius of Cd ion, 0.97 Å,³⁵ is much smaller than the size of S site, Cd²⁺ ions can be easily adsorbed on the surface of S plane. This is the case for Cd²⁺ is dissociated from counter anions. In a precursor solution of CdF₂, Cd²⁺ ion exists naked because the stability constant logK₁ for Cd²⁺ and F⁻ is very small. Furthermore, the protonation of F⁻ is rather strong since pK_a for HF is 3.18.³⁶ On the other hand, for CdI₂, the stability constant is much larger than CdF₂. Since pK_a for HI is -9.5,³⁶ a higher amount of I⁻ ions probably coordinate to Cd²⁺ ion than F⁻. Since the ionic radius of I⁻, 2.16 Å, is larger than that of F⁻, 1.15 Å, coordination of I⁻ to Cd²⁺ may prevent the adsorption of Cd²⁺ on S surface of CdS crystalline. It would be one of the reasons for the observation that CdI₂ gave an amorphous CdS. Since the crystallite radius of Cl⁻ is 1.81 Å³⁵ and it is almost equal to 1.84 Å of S²⁻, Cl⁻ ions can occupy the place of S ions on the Cd layer of the CdS surface. Furthermore, a cross-linking of Cd²⁺ by Cl⁻ can occur both in crystallites and complex ion. Then, adsorbed Cd²⁺ ions may be bridged by Cl⁻ and be stabilized at the surface of the CdS crystal.

The radius of ions may vary depending on the chemical and physical environments where they are located. Even if we employed the atomic radii as

the sizes, the above prediction holds because those of Cl^- and S^{2-} are both 1.00 Å.³⁷ Therefore, from the viewpoint of the ion size, it is supported that CdCl_2 is suitable for the fabrication of thicker crystalline CdS films by the SILAR method.

3.3 The effect of chelating reagents.

Although CdCl_2 was found to be suitable for the fabrication of CdS thin films by the SILAR method, the thickness of the obtained films did not reach 67 nm, which is expected from the ideal atomic layer deposition with 200 cycles. To increase the film thickness we added various chelating reagents into the CdCl_2 solution and tried to change the equilibrium of ionic adsorption at the surface. Figure 4 shows the effects of various chelating reagents on the film thickness, surface roughness, crystallite size, and S/Cd ratio of the composition. In this figure, “None” designates the results obtained in the absence of a chelating reagent. When the XRD peak of CdS was not observed, the crystallite size was not shown in the figure.

Both MEA and Cys are found to increase the film thickness. With respect to the crystallinity, Cys gave a crystallized film, while MEA provides no distinct crystalline peak in XRD analysis. Although a thicker film was obtained with Cys, we could not obtain a flat film. The S/Cd ratio of the films obtained with Cys, EN, and NTA reduced as compared to that without chelating reagent. On the other hand, in the presence of TEOA, the obtained film became thicker, flatter and well crystallized, furthermore the S/Cd ratio was almost stoichiometric as that of “None”. Then, we can conclude that TEOA is the most effective chelating reagent

among the reagents tested for the SILAR method.

The chelating reagent may remain in the CdS film prepared by the SILAR method. If it is the case, the included reagent could be observed as carbon peak in AES spectra. The AES spectra have already been shown in our previous brief report²⁴ for CdS films prepared with and without TEOA, beside the spectrum of authentic single crystal. The shape of the AES spectrum for CdS thin films prepared by the SILAR method with TEOA was identical to that for a single crystalline CdS, and carbon was not detected, indicating that TEOA does not remain in the film. Figure 5 shows a depth profile of AES signal intensities obtained for the CdS film prepared with MEA. At 120 s of the etching time, the signal of In and O of ITO substrate appeared. From surface to this depth, the amounts of S and Cd were constant. In this measurement, carbon was detected in a low level. But this signal originates from a contaminant in the AES apparatus since it was also observed in the region of ITO where carbon does not exist. Thus, it is concluded that chelating reagents and oxygen are not contained in the obtained CdS film.

As stated above we found that the effective chelating reagents are MEA and Cys for the film thickness, and TEOA for the crystallinity and the surface roughness. In order to explain the difference, coordination strength of the chelating reagents is taken into account similarly to the case of the counter anions. The stability constant listed in Table 1 is also used as a measure of the coordination strength. It is likely that the chelating reagent coordinates to the surface Cd atoms, which bound to the three subsurface S atoms of hexagonal

crystal. By forming a tetrahedron with three S ions and L, the Cd ion locates at the stable position without excess adsorption. When L contains mercapto group as the case of MEA and Cys, the films were not crystallized, indicating that the formation of the particles is favorable against the growth of the film. On the other hand, TEOA gave thicker and better crystallized film than “None” without diminution of S/Cd ratio. These observations are explained by the strength of the coordination. The coordination strength of TEOA to Cd ion would be moderate as compared to those of MEA and Cys, then the substitution of S ion for TEOA would occur smoothly because $\log K_1$ of SH^- is larger than that of TEOA as shown in Table 1. Since TEOA is known as a sacrificial reagent to supply electrons,³⁸ this electron donating properties may assist the formation of CdS bond.

Next, we tried to improve the film quality by changing the six cadmium ion sources in the presence of TEOA. As an experimental result, all of the Cd sources gave films showing crystalline properties. Since CdI_2 and $\text{Cd}(\text{ClO}_4)_2$ gave non-crystallized films in the absence of TEOA, this result indicates that the effect of counter ions for I^- and ClO_4^- is reduced by chelating of TEOA to Cd^{2+} . Although CdCl_2 and CdI_2 provided transparent films with TEOA, the other ion sources, CdF_2 , $\text{Cd}(\text{ClO}_4)_2$, $\text{Cd}(\text{CH}_3\text{COO})_2$, and $\text{Cd}(\text{HCOO})_2$ gave only powdery and opaque films. The S/Cd ratio of CdI_2 was 0.99 with TEOA. This value was improved as comparing with 0.75 obtained without TEOA and better also than 0.92 and 0.93 obtained for CdCl_2 with and without TEOA, respectively. Besides, the surface roughness was extremely improved for CdI_2 . Thus, we found that TEOA is the most effective chelating reagent especially for the film crystallization.

3.4 The effect of pH of the Cd solutions

When the films are fabricated by the CBD method, the deposition rate of CdS is generally increased with the pH value of the solution. This is explained by that the formation of monovalent cation CdOH^+ at a higher pH is preferable to fabricate semiconductor thin films from solutions. However, pH of the precursor solution in the SILAR method was not usually adjusted because the additional ionic species possibly prevents the adsorption of ionic reactants on the substrate surface. Therefore, in the present experiment the pH was adjusted only to avoid the precipitation of $\text{Cd}(\text{OH})_2$. In Figure 6, the film properties in Figure 3 are re-plotted against the values of pH of the Cd solutions. The film thickness and the crystallite size are not correlated with pH. The present observation indicates that the coordination of counter ion to Cd^{2+} gives a dominant effect to the growth of CdS films than that of OH^- ions. This conclusion is consistent with the degree of coordination calculated from $\log K_1$ with the concentration of the counter ions.

Figure 7 is a re-plot of Figure 4 against pH of CdCl_2 solutions containing chelating reagents. When Cys or MEA was used as a chelating reagent the obtained CdS became thicker even at a lower pH. The value of pH of Cd ion solution was not correlated with any property of the CdS films obtained, similarly to the case in the absence of the chelating agent. The crystallinity increased just slightly when the pH of CdCl_2 solution with TEOA was increased from 6.6 to 8.8. These results could be also explained by the large stability constant for the ligand

as shown in Table 1.

4 Conclusion

We fabricated CdS thin films by the SILAR method and investigated the effects of deposition cycles, Cd²⁺ ion sources, *i.e.* CdF₂, CdCl₂, CdI₂, Cd(ClO₄)₂, Cd(CH₃COO)₂ and Cd(HCOO)₂, chelating reagents, *i.e.* 2-mercaptoethylamine (MEA), cysteine (Cys), ethylenediamine (EN), triethanolamine (TEOA), monoethanolamine (MEOA), and nitrirotriactic acid (NTA), and pH on the film properties such as thickness, crystallite size, surface roughness, and S/Cd component ratio. We confirmed that the film thickness and the crystallite size increased with increasing the number of deposition cycles. The film properties were not correlated with pH, suggesting that the coordination of chelating reagents and counter ions are larger than that of OH⁻. Carboxyl-group of the Cd sources gave well crystallized films. The formation of crystallite film was discussed in terms of stability constant. The chelating reagents that have a mercapto group coordinates too strong to form flat surface. TEOA improved the thickness without loss of the crystallinity. As far as the overall quality of the films concerns, CdCl₂ and TEOA were found to be the most efficient as a Cd²⁺ ion source and a chelating reagent, respectively.

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Table 1 Values of the stability constants for Cd²⁺ ion

| Ligand | logK ₁ | logK ₁ K ₂ | Reference |
|----------------------------------|---------------------|----------------------------------|-----------|
| (counter ions) | | | |
| Cl ⁻ | 1.57 | 2.26 | 28 |
| F ⁻ | 0.76 | 0.6 | 28 |
| I ⁻ | 2.3 | 3.43 | 28 |
| ClO ₄ ⁻ | <0.7 ^(a) | | 28 |
| CH ₃ COO ⁻ | 1.24 | 1.9 | 29 |
| HCOO ⁻ | 1.04 | 1.23 | 30 |
| (chelating reagents) | | | |
| MEA | 10.97 | 17.1 | 29 |
| Cys | 12.88 | 19.63 | 32 |
| EN | 5.69 | 10.36 | 30 |
| TEOA | 3.15 | | 30 |
| MEOA | 2.77 | 4.09 | 31 |
| NTA | 9.4 | 14.3 | 30 |
| (others) | | | |
| SH ⁻ | 7.6 | 14.6 | 31 |
| OH ⁻ | 4.7 | 7.8 | 28 |

(a) No definite value was available, but it is lower than that of F⁻ ion.

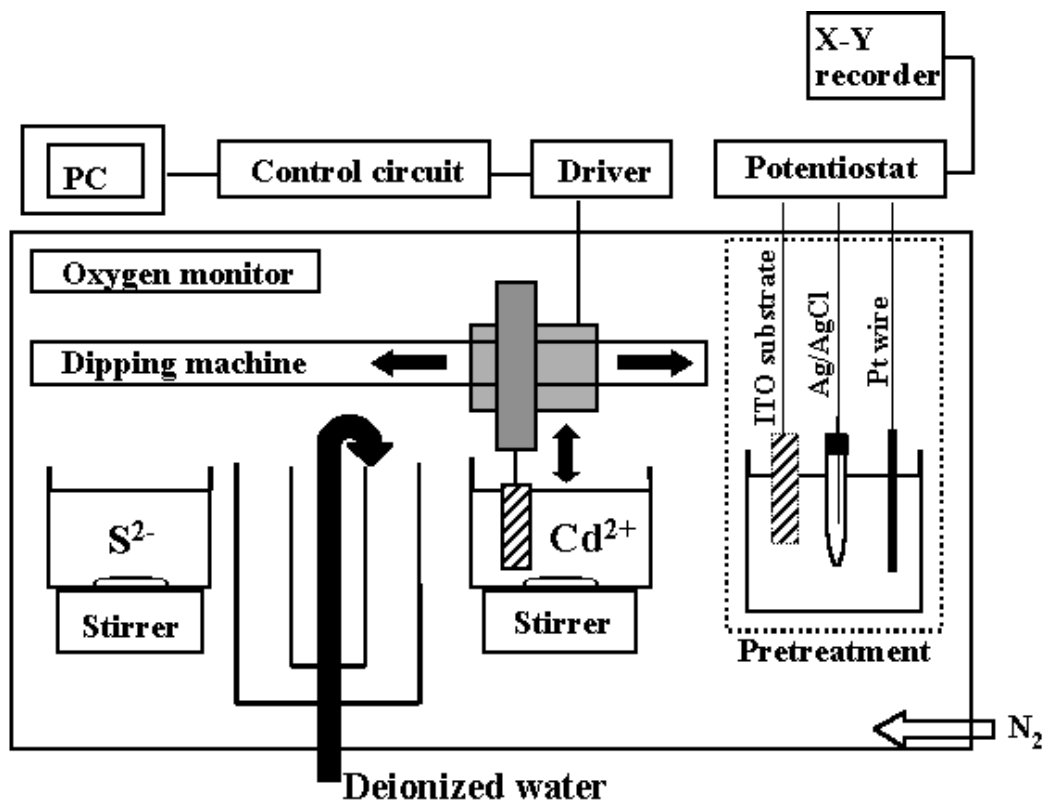


Fig.1. Diagram of the automated dipping system.

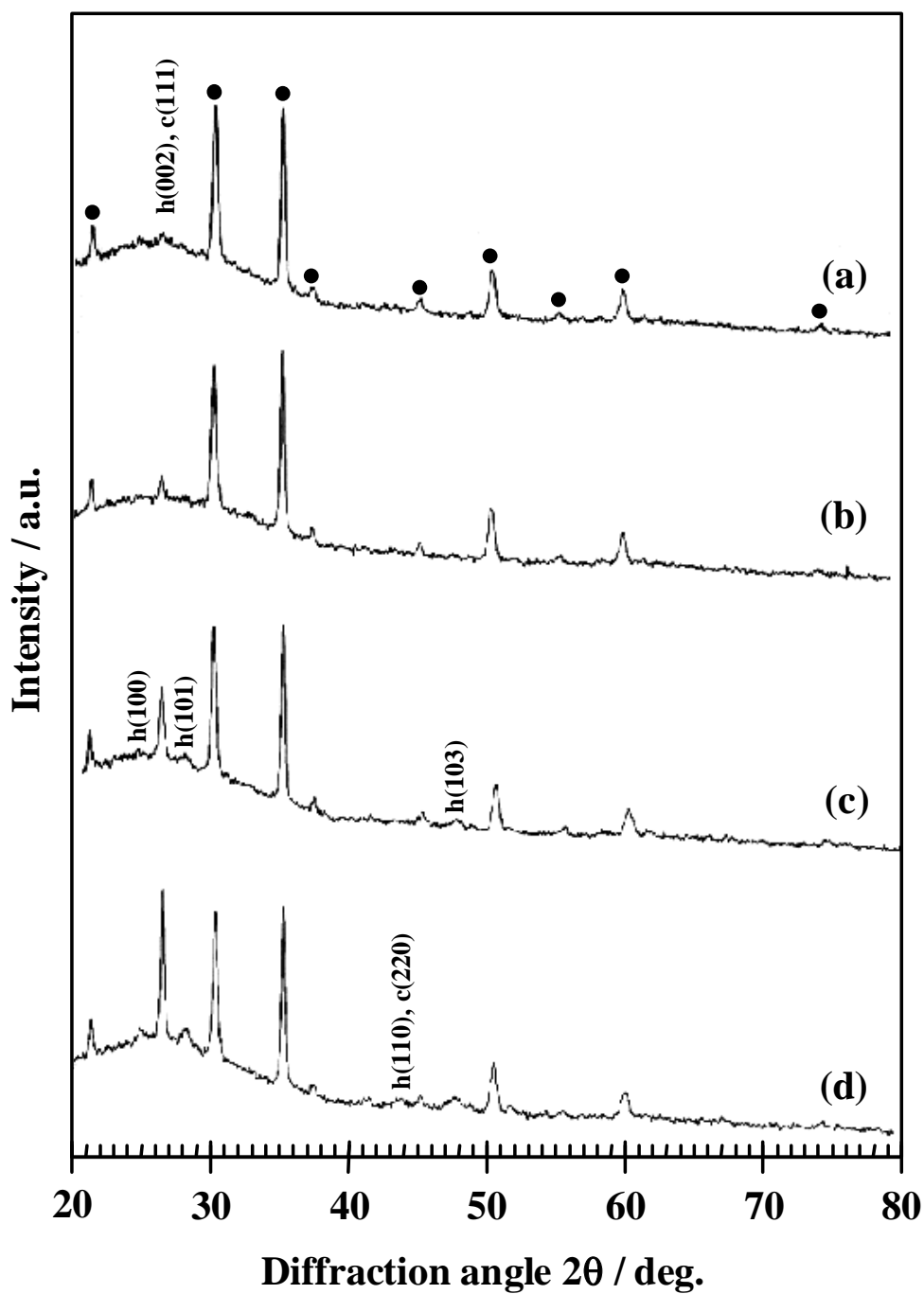


Fig.2. XRD patterns for CdS thin films obtained with (a)200, (b)400, (c)700, and (d)1000 SILAR cycles. h and c indicate hexagonal and cubic, respectively. Peaks marked with • originate from the ITO substrate.

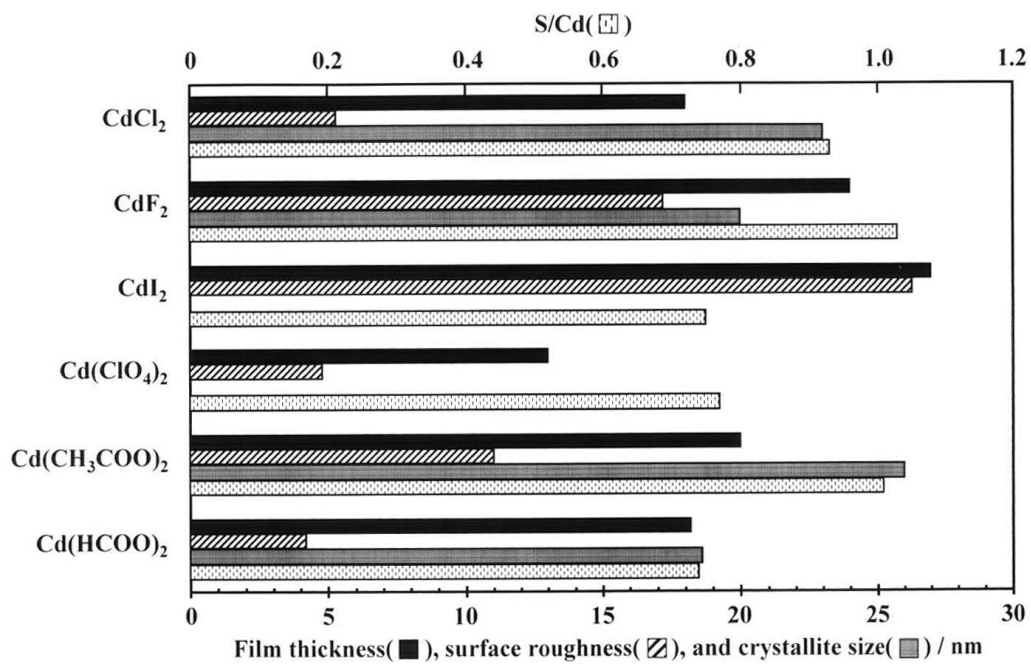


Fig.3. Effect of counter anions of Cd²⁺ on the properties of the film prepared by SILAR method. 0.02 M CdCl₂ and 0.01 M Na₂S solutions were used as Cd²⁺ and S²⁻ sources, respectively. The surface roughness of the substrate was 4.12 nm.

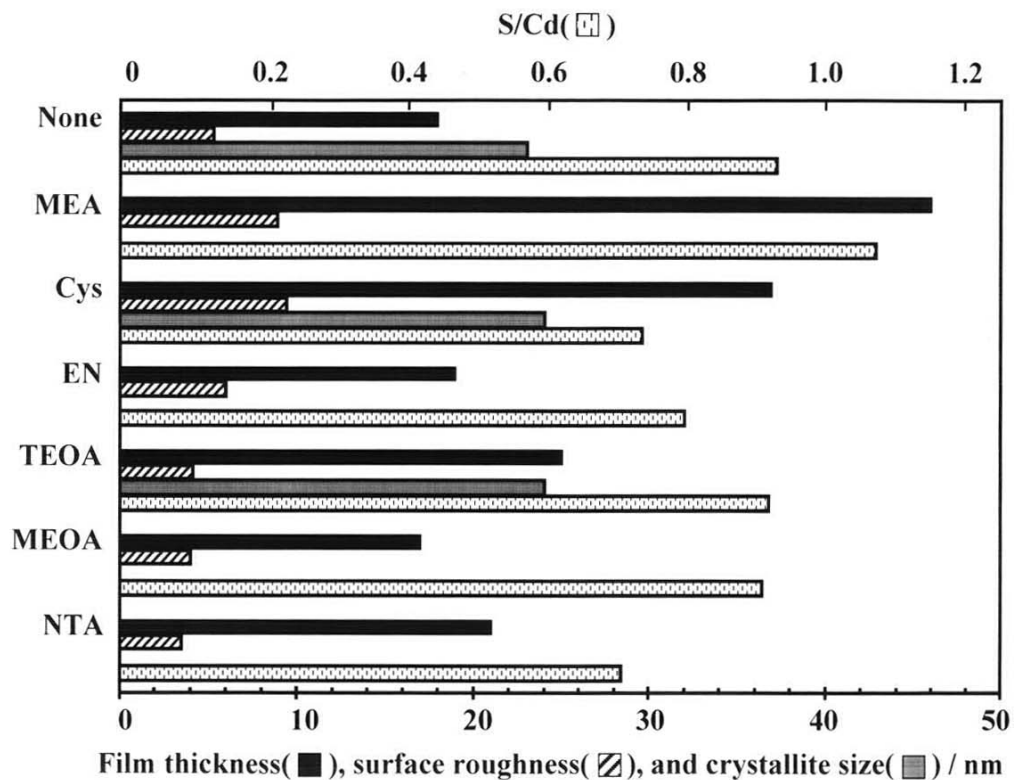


Fig.4. Effect of chelating reagents on the properties of the CdS films prepared by SILAR method with 0.02 M CdCl₂ solution containing chelating reagents of 0.02 M. The surface roughness of the substrate was 4.12 nm.

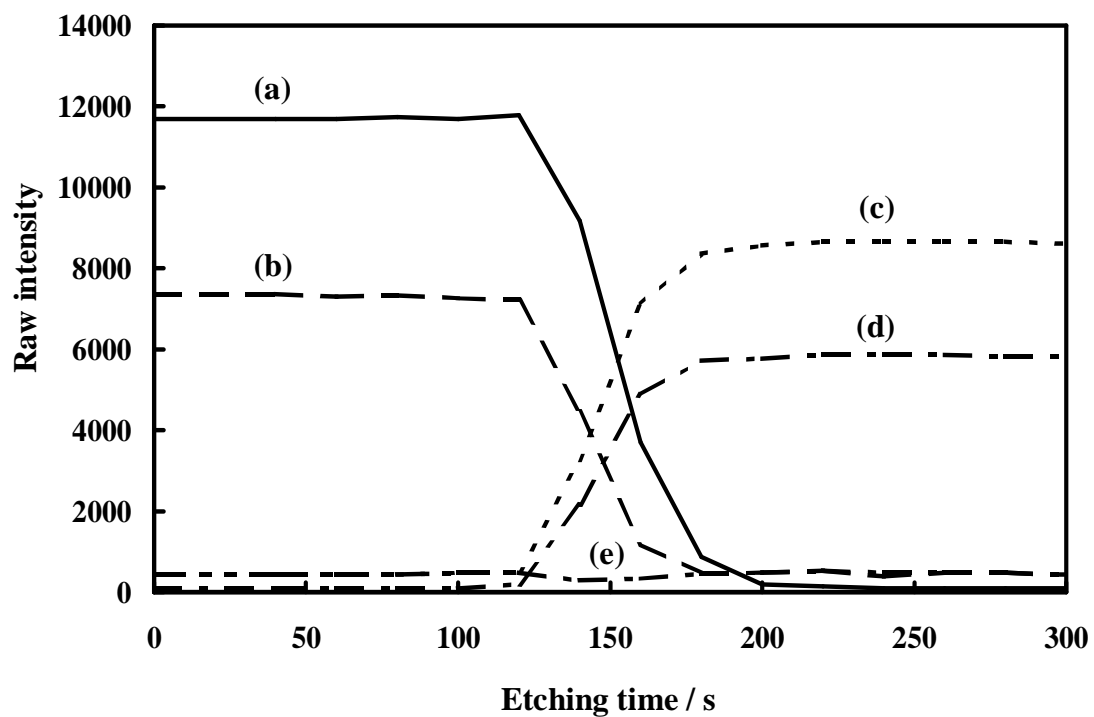


Fig.5. The AES depth profile showing the distribution of (a)S, (b)Cd, (c)In, (d)O, and (e)C in the CdS thin film fabricated by SILAR method using MEA as a chelating reagent. The film thickness was 46 nm.

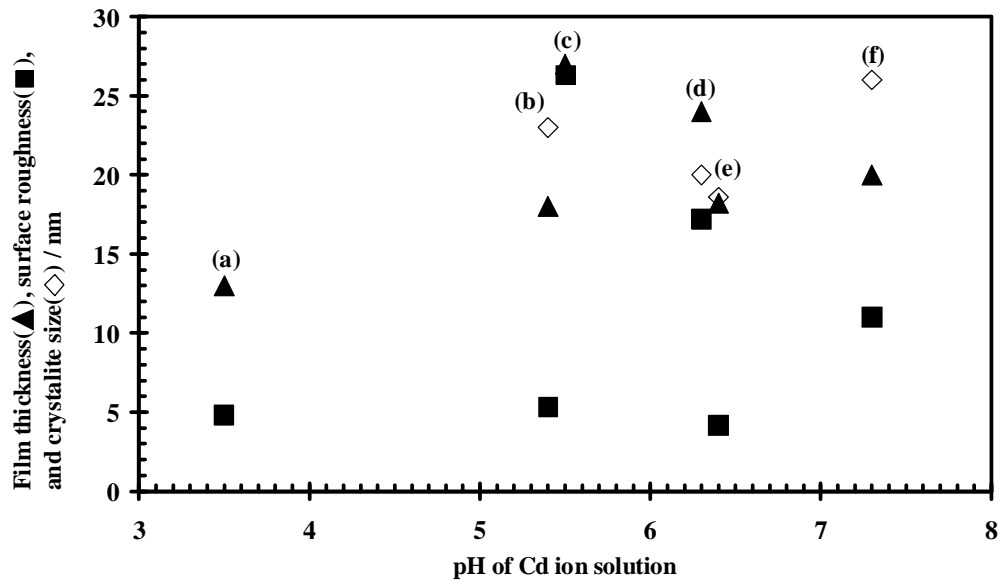


Fig.6. Relationships between characteristics of CdS thin films and pH for several Cd ion sources solutions : (a)Cd(ClO₄)₂, (b)CdCl₂, (c)CdI₂, (d)CdF₂, (e)Cd(HCOO)₂, and (f)Cd(CH₃COO)₂.

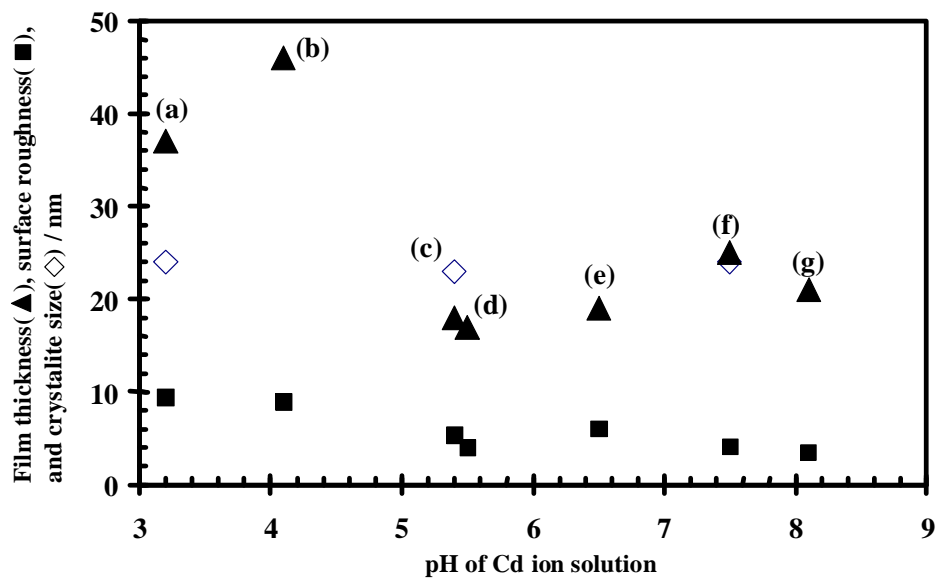


Fig. 7. Relationships between properties of CdS thin films and pH for CdCl₂ solutions as an effect of chelating reagent : (a)Cys, (b)MEA, (c)None, (d)MEOA, (e)EN, (f)TEOA, and (g)NTA.

