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The Role of Electrolyte Components in the Electrodeposition of CdS Films Studied by Cyclic Voltammetry

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The electrodeposition of CdS was conducted in aqueous solution containing $CdSO_4$ and $Na_2S_2O_3$ as sources supplying cadmium and sulfur, respectively. The roles of several additives, comprising $(NH_4)_2SO_4$, NaCl and glycerol were investigated by cyclic voltammetry. The proposed mechanism of the electrodeposition of CdS consists of an adsorption process coupled with a chemical reaction: $Cd^{2+} + S^{2-} \longrightarrow CdS$ and/or an adsorption process coupled with an electron transfer reaction: $Cd^{2+} + S + 2e^- \longrightarrow CdS$. The presence of all such additives enables the adsorption processes and the electron transfer reaction to take place at the potentials positive of −0.8 V, thereby promoting the formation of CdS; in addition, the undesired electrodeposition of Cd was suppressed.

Key Words : Electrodeposition, CdS, Adsorption, Cyclic Voltammetry, Coupled Reaction

1 Introduction

II-VI semiconductors such as CdS, whose optical band gap is 2.42 eV, could be fabricated by electrodeposition from aqueous solutions, under various conditions.[1-3] In these works, CdS films were prepared either in a two-electrode cell with an alternating current voltage, or in a three-electrode cell with a controlled rectangular wave potential in order to improve the film quality. As reported,[1] an aqueous solution consisting of $CdSO_4$ and $Na_2S_2O_3$ as sources supplying cadmium and sulfur, respectively, and a set of other reagents examined, comprising NaCl, $(NH_4)_2SO_4$ and glycerol, play a role as additives (see Table 1). However, what is the intrinsic role of each additive and what are the mutual interactions of the components have still not been clarified. In particular, this is because the sources supplying sulfur consist of $S_2O_3^{2-}$ and SO_4^{2-} and the overall process is conducted via two routes, a chemical reaction[1] 1, and the electrochemical reactions[4] 2 and 3:

$$S_2O_3^{2-} + H^+ \longrightarrow S + H_2SO_3 + H_2O \qquad (1)$$

$$S_2O_3^{2-} + 6H^+ + 8e^- \longrightarrow 2S^{2-} + 3H_2O\ ;\quad E^0 = -0.006\ \mathrm{V\ vs.\ NHE} \qquad (2)$$

$$SO_4^{2-} + 10H^+ + 8e^- \longrightarrow H_2S + 4H_2O\ ;\quad E^0 = +0.303\ \mathrm{V\ vs.\ NHE} \qquad (3a)$$

$$SO_4^{2-} + 8H^+ + 6e^- \longrightarrow S + 4H_2O\ ;\quad E^0 = +0.357\ \mathrm{V\ vs.\ NHE} \qquad (3b)$$

Table 1 Solution composition for CdS electrodeposition.[1] Mixed at the volume ratio A:B = 1:3.

"A" solution (cadmium source)	0.01 M $CdSO_4$ 0.17 M $(NH_4)_2SO_4$ 0.01 M glycerol
"B" solution (sulfur source)	0.35 M $Na_2S_2O_3$ 0.75 M NaCl

Thus, the formation of CdS films via the electrochemical approach is expected to be rather complex, involving a chemical step and an adsorption step coupled with the electron transfer reaction.

Cyclic voltammetry (CV) has been well known to be an excellent analytical technique, which can control the programmable delivery of electrons through the electrode surface and the potential applied to the electrode. CV studies allow us evaluate the thermodynamic and kinetic parameters of a redox system occurring at an electrode surface. In itself, it is also able to provide a variety of routes in various types of programmed control of potential in the preparation of film semiconductors. The present work shows that CV studies and the useful information that they provide can greatly help to elucidate the influences of electrolyte components on the formation of CdS.

2 Experimental

Cyclic voltammetry studies were carried out in a three-electrode glass cell containing electrolyte solution. A platinum sheet with a surface area of 0.1 cm^2 served as the working electrode, and an Ag/AgCl (4 M KCl) reference electrode was used. Before each measurement, the platinum working electrode was sonochemically cleaned in acetone, and then activated in 0.05 M H_2SO_4 with a potential sweep from −1.5 V to +1.5 V for 15 cycles, at scanning rate of 50 mV/s.

For studying the role of each component, the 0.01 M $CdSO_4$ solution was chosen as the base solution, and then other components were added to this base solution

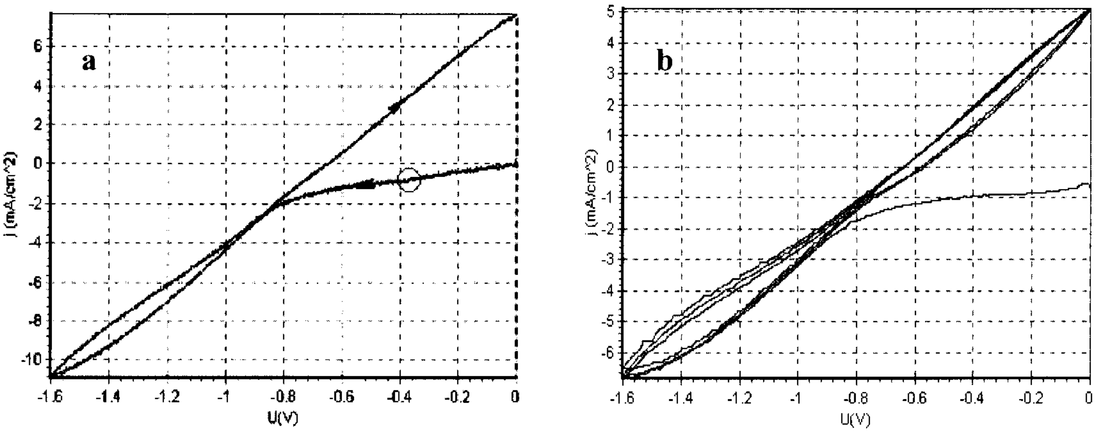

Fig. 1 Cyclic voltammograms of (a) 0.01 M $CdSO_4$ solution (Cd solution) and (b) 0.01 M glycerol-containing Cd solution (Cd-gly solution).

one by one, with the concentrations listed in Table 1. For the preparation of solutions, all chemicals, which were supplied by Merck, were dissolved in triply distilled water to the required concentrations for each component, and the pH was adjusted to 3.1 with 1 M H_2SO_4 solution. The electrolyte solutions were bubbled with nitrogen gas for 30 min before and during the electrochemical measurements to remove O_2 from the solution.

The CV studies were carried out by use of an EG&E PAR potentiostat model 362 with a programmer (Ecunive HH-5). The CV measurements for the various kinds of solution were performed at a sweep rate of 100 mV/s unless otherwise noted. The surface morphology of the film was observed with a JEOL scanning electron microscope (SEM), model JSM-5410 LV. The elemental composition was measured by Auger electron spectroscopy (AES) with a JAMP-10SX spectrometer (JEOL Inc.).

3 Results and Discussion

3. 1 Effect of glycerol

Figure 1 shows a CV conducted in 0.01 M $CdSO_4$ solution (noted as Cd solution). As marked with a circle in Fig. 1, at potential of −0.38 V there exists a change in the slope of the cyclic voltammogram, and the current at potentials in the range from −0.38 V to −0.45 V appeared to be constant. This may be due to desorption of sulfate anions (SO_4^{2-}) from the electrode surface, by increasing the electrostatic propulsive forces between the anionic charge and the negatively polarized electrode, and substituting by adsorption of Cd^{2+} and H_2O molecules (adsorption of H_2O molecules may give rise to the oxygen AES signal seen Fig. 6). The flow of electrons delivered to the metallic electrode surface increases at this point and appears to be just charging the double layer. Also, in the potential range from −0.38 V to −0.80 V, there may exist several kinds of adsorbed complexes of cadmium cations and water molecules, as will be discussed in the following paragraph. The reduction of cadmium cations to metallic atoms is considered to start at a potential of −0.82 V, at which the cathodic current increased significantly. As shown in Fig. 1b, addition of glycerol into this solution (Cd-gly solution) produces no change in the appearance of the CV. The reduction of cadmium cations still starts at a potential of −0.82 V, meaning that no special complex formation of cadmium cations with glycerol molecules takes place. However, the cathodic current (Fig. 1b) of cadmium at a potential range from −0.82 V to −1.6 V is less than that in glycerol-free solution (Fig. 1a). This may be due to a shielding of the electrode surface by glycerol molecules, decreasing the electrostatic attraction of other additives to cadmium cations. Whereas, in the potential range from −0.82 V to 0.0 V, the higher current (in comparison of Fig. 1b to Fig. 1a), which appears to exhibit the delivery of electron just charging the double layer, is evidencing the adsorption of glycerol molecules on the electrode surface, then causing the shielding as mention.

Also, the slope of the CV in the range from −0.85 V to −1.1 V appears to constant, suggesting that in this potential range, only the reduction of cadmium cations to cadmium atoms occurs. At a potential of about −1.1 V, the slope of the branch of the cathodic sweep changes gradually, showing the beginning of the reduction of water molecules:

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- ;\quad E^0 = -0.83 \text{ V vs. NHE}^{5)} \qquad (4)$$

By reaction 4, the OH^- concentration in the double layer increases, and it participates in the formation of complexes, $[Cd(OH)_n(H_2O)_x]^{(2-n)+}$ ($n=1$; 2), leading to a decrease in Cd^{2+} concentration, thus decreasing the reduction of Cd^{2+}. In addition, the standard redox potential E^0 of $Cd(OH)_2$ is −0.82 V vs. NHE[5]:

$$Cd(OH)_2 + 2e^- \longrightarrow Cd + 2OH^- ;\quad E^0 = -0.82 \text{ V vs. NHE} \qquad (5)$$

This redox potential is comparable to that of water molecules, while it is much more negative than that for the Cd^{2+} cation (−0.4 V vs. NHE). Thus, by repeating the cathodic sweep from −1.1 V to −1.6 V, the slope of the CV (Fig. 1a) gradually decreases. When various ligands are added, they can form complexes with Cd^{2+}, since their equilibrium constants are significantly different from those of $[Cd(OH)_n(H_2O)_x]^{(2-n)+}$ complexes.

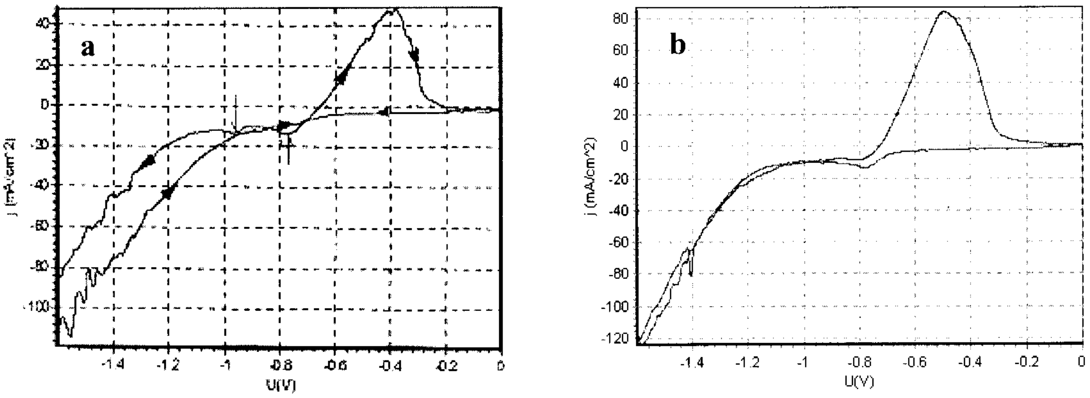

Fig. 2 Cyclic voltammograms of (a) Cd solution containing 0.17 M $(NH_4)_2SO_4$ (Cd-Am solution) and (b) 0.01 M glycerol-containing Cd-Am solution (Cd-Am-gly solution).

Thereby, new complexes of Cd^{2+} and $[Cd(OH)_n(H_2O)_x]^{(2-n)+}$ will be reduced at different potentials. Consequently, there arise considerable changes in the shape of the CV with appearance of local peaks evidencing the presence of such new complexes (see below).

As mentioned above, glycerol molecules work as a shield on the electrode surface and also attract cadmium cations. Indeed, consideration of the cyclic voltammograms in Figs. 2a plus 4a shows that the presence of other additives, such as $(NH_4)_2SO_4$ (Fig. 2a), NaCl (Fig. 3a), or both (Fig. 4a) caused obvious changes in the shapes of the CVs and the appearance of local cathodic peaks during a negative potential sweep. However, when glycerol was added, the CV curves became smoother than before in the potential range of -1.6 V to -0.6 V, in which cadmium species can be discharged. In this potential range the branches of the cathodic and anodic potential sweeps are close together (see Figs. 2b plus 4b in comparison with Figs. 2a plus 4a). In particular, the potentials, at which cadmium species were discharged, in general, shifted to more positive values. This once again supports the existence of the attraction of glycerol molecules and cadmium cations. Such attraction partly reduced the influences of other additives, and the cathodic current increased.

Due to the addition of glycerol, the CV curve of Cd-Am-gly solution (Fig. 2b) became also smoother than that of Cd-Am solution (Fig. 2a). Of course, the disappearance of a cathodic peak at -0.96 V and there is just still a cathodic peak at -0.76 V, both of which appear to show that in Cd-Am-gly solution there has one kind of complex of cadmium and ammonium, $[Cd(NH_3)_4]^{2+}$ complex, is predominant in a suppression of $[Cd(NH_3)_6]^{2+}$ complex. This is evidencing a shielding of glycerol to produce $[Cd(NH_3)_4]^{2+}$ complex, which is also an advantage for the matching of Cd^{2+}, S and S^{2-} to yield CdS, when $Na_2S_2O_3$ is added (see 3.4).

3. 2 Effect of ammonium ions

When 0.17 M $(NH_4)_2SO_4$ was added into Cd solution (denoted as Cd-Am solution), since the molar ratio of ammonium and cadmium cations was 34:1, almost all of the cadmium cations existed in the complexed form with ammonia, which is reduced as follows:

$$[Cd(NH_3)_4]^{2+} + 2e^- \longrightarrow Cd + 4NH_3\ ; \quad E^0 = -0.61 \text{ V vs. NHE}^{5)} \qquad (6)$$

The presence of ammonium inhibits the formation of $[Cd(OH)_n(H_2O)_x]^{(2-n)+}$ complexes. Also, the existence of ammonium ions in solution will promote the complete dissolution of electrodeposited cadmium during the anodic potential sweep, giving rise to the anodic wave before the anodic current reaches zero at zero potential (Fig. 2a). A significant feature of the CV conducted in Cd-Am solution is this asymmetric anodic wave centered at a potential of about -0.4 V in the positive sweep from -1.6 V to 0.0 V. On the other hand, in the negative sweep from 0.0 V to -1.6 V, the reduction of cadmium cations is considered to start at $E = -0.71$ V, more positive than those of the previously mentioned solutions (Cd and Cd-gly). A striking point, however, here is the rise of two cathodic peaks located at -0.76 V and -0.96 V (indicated with arrows in Fig. 2a). This may be attributed to the reduction of complexes, such as $[Cd(NH_3)_4]^{2+}$ and $[Cd(NH_3)_6]^{2+}$. During the dissolution of the electrodeposited cadmium, the complexes $[Cd(NH_3)_4]^{2+}$ and $[Cd(OH)_n(H_2O)_x]^{(2-n)+}$ are likely formed, and thus the local anodic peaks located at potentials of -0.48 V, -0.41 V, -0.38 V and -0.32 V could be observed, as shown in Fig. 2a.

Comparison of Fig. 2 with Fig. 1 shows that the copresence of ammonia and glycerol has a positive effect on the electrodeposition of cadmium. In both cases in Fig. 2, the anodic wave appeared in the potential range from -0.8 V to -0.2 V, before the anodic current reached zero at $E = 0.0$ V. This observation is quite different from that shown in Fig. 1, in which the current did not reach zero at $E = 0.0$ V in the positive sweep. In particular, the electrodeposition of cadmium can come from reactions 5 and 6 and others, as follows:

$$Cd^{2+} + 2e^- \longrightarrow Cd\ ; E^0 = -0.402 \text{ V vs. NHE}^{5)} \qquad (7)$$

By these reactions (5-7), the Cd film is formed at the cathode surface. The films seem to dissolve completely in the following anodic sweep, suggesting that the electrodeposited cadmium metal is in the form of very fine

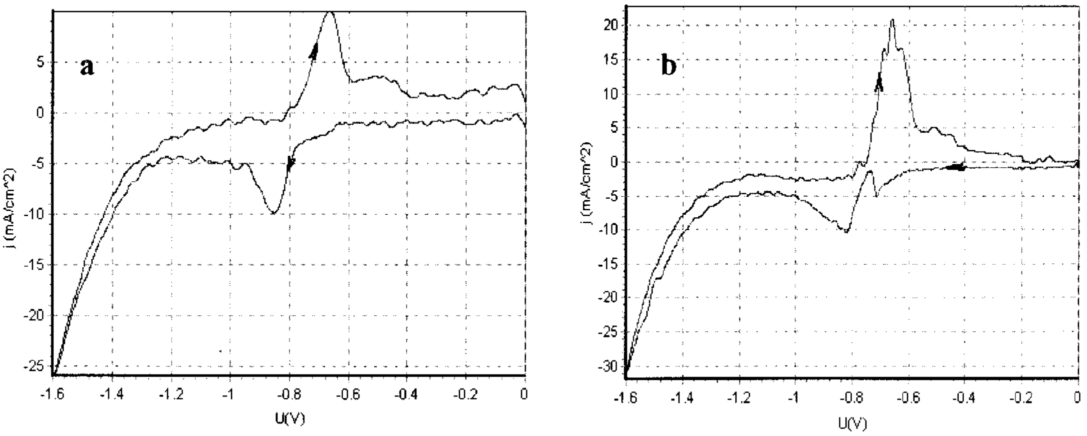

Fig. 3 Cyclic voltammograms of (a) Cd solution containing 0.75 M NaCl (Cd-NaCl solution) and (b) 0.01 M glycerol containing Cd-NaCl solution (Cd- NaCl-gly solution).

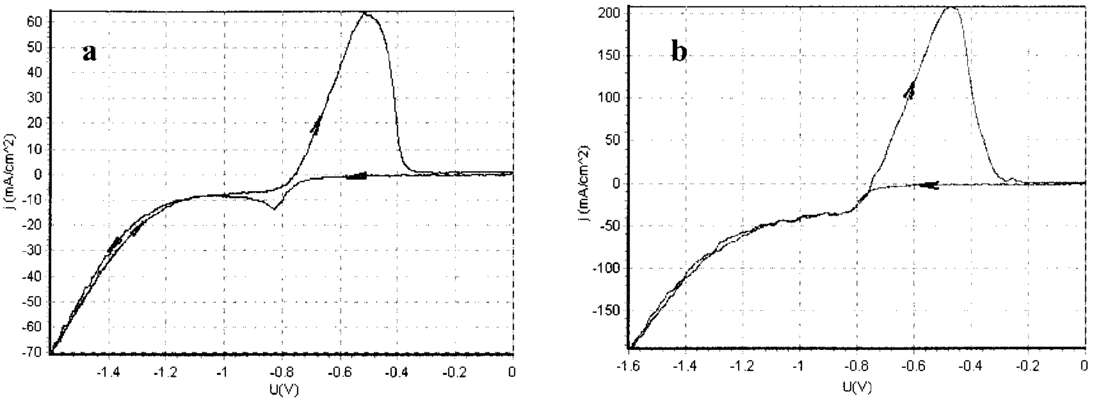

Fig. 4 Cyclic voltammograms of (a) Cd-NaCl solution with 0.17 M $(NH_4)_2SO_4$ (Cd-Am-NaCl solution), and (b) 0.01 M glycerol containing Cd-Am-NaCl solution (Cd-Am-NaCl-gly solution).

particles and is thus very easy to dissolve, forming complexes with ammonia. This is one of several experimental factors, on the basis of which we can prepare the smooth CdS films. Of great interest is the fact that, in the initial positive sweep, from -1.6 V to 0.0 V, the cathodic current at -1.2 V decreases from 40 mA/cm^2 in Cd-Am solution (Fig. 2a) to 20 mA/cm^2 in Cd-Am-gly solution (Fig. 2b). At more positive potentials, ranging from -1.1 V to -0.79 V, the current was almost constant, at about 10 mA/cm^2 (Fig. 2b), and the same in both potential sweeps (positive and negative sweeps). Meanwhile, the cathodic currents observed in Cd-Am solution (Fig. 2a) were different for both directions of potential sweep. This is one of the observations, that help us to understand why the preparation of CdS films was carried out at a potential of -1.0 V or -1.1 V,[1, 2] in the combined presence of ammonium and glycerol.

3. 3 Effect of NaCl

To increase the conductivity, 0.75 M NaCl (sodium chloride) was added to the four kinds of solutions used in Figs. 1a and 2b, and the corresponding CVs are shown in Fig. 3a and 4b. Much useful information concerning the mechanism of the cadmium electrodeposition was also obtained. As seen in Fig. 3a, the current is mostly constant and non-Faradaic in the cathodic sweep from 0.0 V to -0.65 V. With further negative sweep, the slope changed suddenly; that is, the cathodic current increased considerably. Two cathodic waves appeared in the potential range from -0.6 V to -1.0 V, suggesting that the reduction of Cd^{2+} to Cd is not as simple as reaction 7. More clearly, due to the presence of glycerol (Fig. 3b), two separated local cathodic peaks, located at -0.72 V and -0.82 V, are considered as obvious evidence to confirm the two-step reduction of Cd^{2+} . Also, the anodic wave separated into one intense peak located at a potential of -0.66 V and three weak anodic peaks located at -0.77 V, -0.72 V and -0.66 V. This signifies that the dissolving of the electrodeposited Cd film may consist of the one-step process, $Cd \longrightarrow Cd^{2+}$, and the two-step process, $Cd \longrightarrow Cd^{+} \longrightarrow Cd^{2+}$. The dissolution, thus, is proposed to occur as follows:

$$Cd + nH_2O - e^- \longrightarrow Cd(OH)(H_2O)^{(n-1)+} + H^+ - e^- \longrightarrow [Cd(OH)_x(H_2O)_{(n-x)}]^{(2-x)+} + xH^+ \quad (8)$$

For the Cd-Am-NaCl solution, which contains ammonium and NaCl, the positive sweep branch and the negative sweep branch almost coincide in the potential range from -1.0 V and -1.6 V (Fig. 4a). This potential range is also expanded from -0.76 V to -1.6 V by addition of glycerol (Fig. 4b), and the cathodic current increased considerably, but the cathodic peak disappeared. Thus, the electrodeposition of cadmium may be considered independently to the evolution of hydrogen, even though

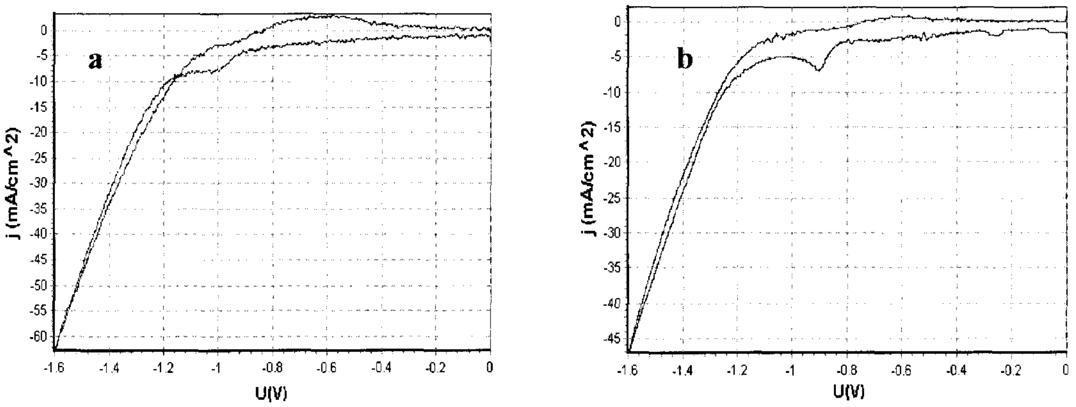

Fig. 5 Cyclic voltammograms of Cd solution containing $Na_2S_2O_3$, (Cd-$Na_2S_2O_3$ solution) at scan rates of (a) 100 mV/s and (b) 10 mV/s.

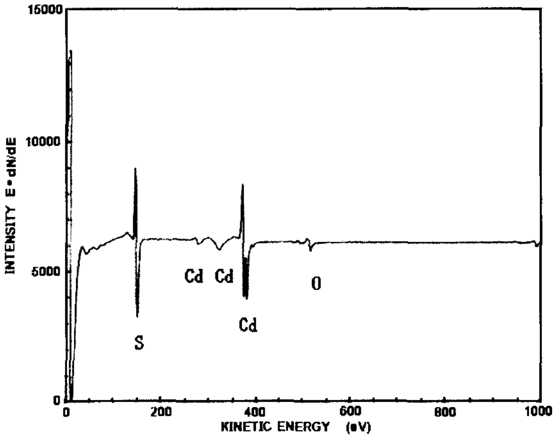

Fig. 6 Auger electron spectrum of CdS film on Pt electrode measured after argon ion etching for 30 s. This CdS film had been prepared in a solution containing 0.01 M $CdSO_4$ and 0.35 M $Na_2S_2O_3$, under conditions of $E_H = 0$ V (6 seconds), $E_L = -1.1$ V (6 seconds), for 20 repetitions.

both processes occur simultaneously. Thus, the amount of cadmium species adsorbed for the formation of nuclei increases strongly, leading to the easier formation of very fine CdS crystals when sulfur-containing-compounds are added.

3. 4 Formation of CdS with $Na_2S_2O_3$

The presence of $Na_2S_2O_3$ will make possible a new reaction, and the product obtained for the electrode process is quite different from that in the absence of $Na_2S_2O_3$ (Fig. 1a). As seen in Fig. 5a, the anodic current during positive potential sweep in Cd-$Na_2S_2O_3$ solution decreased significantly, a faint broad anodic wave was obtained, and also it reached zero at a potential of 0 V. The electrodeposited product probably consisted of CdS and Cd. As the potential scan rate was decreased down to 10 mV/s, a cathodic peak at about -0.9 V (Fig. 5b), attributable to the reduction of Cd^{2+} to Cd appeared. However, Auger electron spectra were measured for the CdS film electrodeposited on a Pt electrode (Fig. 6) showed that the elemental ratio for S/Cd was 0.82 at the surface and became 0.93 when the surface was argon-ion etched for 30 seconds. An oxygen signal was observed even for the etched sample, indicating that the oxide of cadmium was formed. Contaminant oxygen gas present in the electrolysis solution may cause the formation of oxide.

On the other hand, the formation of S^{2-} coming from reaction 2 starts at a potential of about -1.0 V (Fig. 7a). Thereby, an issue that arises is how to keep Cd^{2+} cations from reducing until S and S^{2-} formation can start with reactions (1-3). This is because the CdS film production can be performed in two processes, one consisting of an adsorption process coupled with a chemical reaction:

$$Cd^{2+} + S^{2-} \longrightarrow CdS \qquad (9)$$

and the other consisting of an adsorption process coupled with an electron transfer reaction:

$$S + Cd^{2+} + 2e^- \longrightarrow CdS \qquad (10)$$

CV studies for all of the additives used, NaCl, $(NH_4)_2SO_4$ and glycerol, showed that just NaCl and $(NH_4)_2SO_4$ suppressed the reduction of Cd^{2+} to Cd, as observed with the disappearance of the anodic wave. The presence of $(NH_4)_2SO_4$ caused the formation of S^{2-} (by reaction 2) to start at a potential of about -0.8 V (Fig. 7b), which is more positive than that observed before (about -1.0 V, Fig. 7a). This means that, at potentials more positive than -0.8 V, sulfur atoms and $S_2O_3^{2-}$ can be adsorbed on the electrode surface. Also, at these potentials, adsorbed cadmium cations can start to be reduced to make the matching of Cd^{2+}, S and S^{2-} for the formation of CdS by reactions 9 and 10. As mentioned above, the addition of glycerol to solutions containing additives other than $Na_2S_2O_3$ has a positive influence on the reduction of Cd^{2+} (Figs. 3 and 4), but, in the cases of solutions containing $Na_2S_2O_3$ without $CdSO_4$, the presence of glycerol has no such influence on the formation of S^{2-}, therefore avoiding excess S^{2-}, which can be oxidized to colloidal S at potentials more positive than the standard redox potential of following reactions:

$$2S^{2-} \longrightarrow S_2^{2-} + 2e^- \ ; E^0 = -0.524 \text{ V vs. NHE}^{4)} \qquad (11)$$
$$S_2^{2-} \longrightarrow 2\,S + 2e^- \ ; E^0 = -0.476 \text{ V vs. NHE}^{4)} \qquad (12)$$

This is very important when the potential applied to

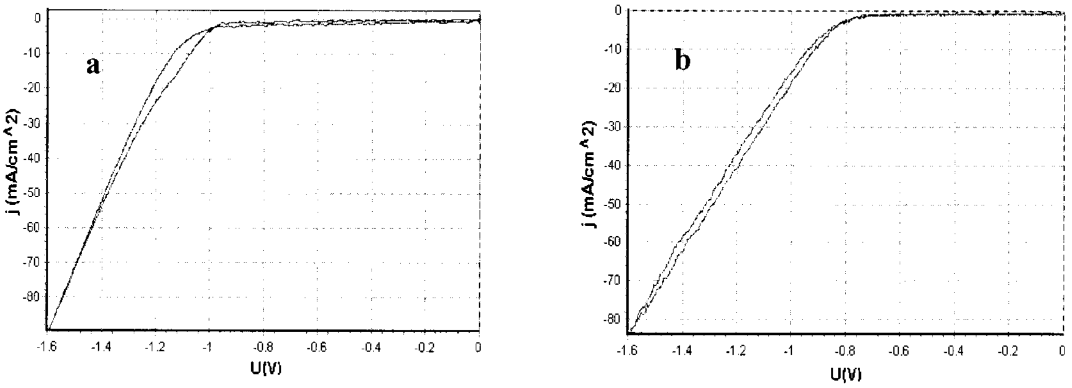

Fig. 7 Cyclic voltammograms of (a) 0.35 M $Na_2S_2O_3$ aqueous solution and (b) $Na_2S_2O_3$ solution containing $(NH_4)_2SO_4$.

Fig. 8 SEM photograph of the CdS film electrodeposited on a platinum sheet in the standard solution (see Table 1), under conditions of $E_H = 0$ V (6 seconds), $E_L = -1.1$ V (6 seconds), for 5 repetitions; scale bar, 1 μm.

the electrode is alternatively changed between $E_L = -1.0$ V and $E_H = 0.0$ V, a regime usually used for the formation of CdS in aqueous solution.[1-3] Also, glycerol can reduce the diffusion of colloidal sulfur resulting from chemical reaction 1 in the bulk of solution to the electrode surface. The adsorption of colloidal sulfur is not responsible for the reaction 10, which requires the sulfur atom, but not colloidal sulfur. To further improve the matching of all components for the formation of CdS, the ratio between them can be adjusted, as shown in Ref. 1. Consequently, the reddish-brown CdS film consisting of particles ranging in size from 50 nm to 80 nm was electrodeposited, as shown in Fig. 8.

4 Conclusions

The above discussions shows that cyclic voltammetry should be considered as a simple, but very useful, technique to investigate and estimate the role of each component of the electrolyte, as well as their mutual influences on the electrodeposition of CdS film, as listed below.

- The mechanism of the formation of CdS film should involve the adsorption processes coupled with a chemical reaction and/or electron transfer reactions.
- The presence of either $(NH_4)_2SO_4$ or NaCl shifts the reduction potential of Cd^{2+} to Cd to start at a potential of -0.70 V (Fig. 2) or of -0.60 V (Fig. 3), which is more positive than that in their absence (-0.82 V; see Fig. 1); the result is a two-step process consisting of a single electron transfer followed by another single electron transfer. Also these additives cause the formation of S^{2-} to start at -0.80 V (Fig. 7b), which is more positive than that in their absence (Fig. 7a). Consequently, at the potentials, at which Cd^{2+} cations can be reduced, sulfur atoms can be adsorbed, leading to the promotion of the formation of CdS, by reactions 9 and 10.
- Glycerol has a positive influence on the reduction of Cd^{2+} and the matching mentioned above may promote the formation of CdS via an adsorption process coupled with an electron transfer reaction 10. Also the presence of glycerol limited the diffusion of sulfur atoms formed in the bulk of solution to the electrode surface, contributing to minimizing the adsorption of colloidal sulfur on the CdS films obtained.

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