Multiple Fabrications of Crystalline CdS Thin Films from a Single Bath by EICD in Acidic Aqueous Solution of Cd^{2+} and Thiourea Complex

Koichi Yamaguchi, Pragati Mukherjee,[†] Tsukasa Yoshida, and Hideki Minoura*
Environmental and Renewable Energy Systems (ERES) Division, Graduate School of Engineering,
Gifu University, 1-1 Yanagido, Gifu 501-1193
[†]*Department of Physics, Alipurduar College, Jalpaiguri 736 122, W. B., India*

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Multiple fabrications of crystalline CdS thin films have been realized by electrochemically induced chemical deposition (EICD) from a single acidic aqueous bath of stable Cd^{2+}–thiourea complexes. Repeated depositions up to five times from the same bath have been proven to yield CdS thin films with essentially the same quality and thickness, owing to the absence of chemical decomposition of the precursor.

Techniques for the preparation of inorganic compound thin films in aqueous solutions have been widely studied in recent years because of their advantages in economical and ecological aspects, as compared to the conventional gas phase techniques which require much energy for the film processing.[1–3]

Solution phase processing of CdS thin films has been achieved by alkaline chemical bath deposition (CBD)[2] typically using thiourea (TU) as S^{2-} source and electrodeposition (ED)[3] in acidic baths containing thiosulfate (TS) whose electroreduction generates S^{2-}, both of which, however, are affected by inclusion of solid particles formed in the bulk of the solutions due to the chemical unstableness of TU and TS. In an attempt to overcome such problems with the previous methods, we have recently developed a new method called electrochemically induced chemical deposition (EICD), by which an atomic layer-by-layer growth of CdS is promoted by electrochemical consumption of proton at the substrate in acidic chemical bath containing Cd^{2+} and thioacetamide (TAA).[4,5] Although chemical formation of CdS particles in solution does occur in such a system, it does not contribute to the film growth, thus achieving a long range homoepitaxial growth of highly crystallized CdS thin films. However, the loss of precursor by formation of the particles can still be regarded as a drawback of this method, making the bath usable only one time, same as in the case of CBD and ED.

Although TU readily decomposes in alkaline solution as it is employed as the key reaction in the CBD of CdS,[2] we have found that TU is fairly stable in acidic solutions. If the composition of the bath is unchanged during the film deposition, repeated use of the bath should be possible. We have attempted EICD of CdS thin films from acidic baths containing TU instead of TAA and discovered that multiple fabrications of CdS thin films with high crystallinity and structural homogeneity from a single bath are indeed made possible.

Doubly distilled and ion exchanged water was used in all the experiments. Aqueous mixed solution of 0.10 M (M = mol dm^{-3}) cadmium chloride and 0.15 M TU served as the deposition bath. Its pH was adjusted to ca. 3.3 by adding appropriate amount of HCl. Argon gas was passed through the bath before the film deposition. An indium tin oxide (ITO) coated glass substrate was degreased sequentially with detergent and acetone, etched in 1 M HNO_3 for 1 min, and finally rinsed with water. A single compartment cell was used, which was equipped with three electrodes, an ITO glass, a Pt wire and a self-made Ag/AgCl (potential = +0.196 V vs NHE) as working, counter and reference electrodes, respectively. The EICD of CdS thin films was performed while potentiostatically cathodizing an ITO working electrode at –0.63 V in the bath maintained at 80 °C. At this potential, a cathodic current of about a few tens of $\mu A cm^{-2}$ is generated due to the electroreduction of proton, which has been found to trigger the film growth in the previous study.[4] The bath was not stirred during the deposition. Passed charge was monitored by a digital coulometer. The X-ray diffractograms (XRD) of the deposited films were recorded on an X-ray diffractometer with Cu Kα radiation. The surface morphology of the films was observed by a scanning electron microscope (SEM). The film thickness was determined by a surface profilometer. Absorption spectra of deposition baths were measured by a spectrophotometer.

After the electrolysis at –0.63 V (vs Ag/AgCl) for 6 h, a well-adherent and transparent film was deposited. It should be noted that the film was not deposited when a substrate was simply immersed in the deposition bath. The film did not grow further after the cathodic electrolysis was terminated. These suggest that continuous electrolysis is necessary for the film growth as found in the previous study.[4]

Table 1. Passed charge and film thickness for 5 runs of CdS thin-film deposition from a single bath[a]

Run	Passed charge / mC cm^{-2}	Film thickness / nm
1	0.302	142
2	0.298	134
3	0.287	132
4	0.289	135
5	0.289	137

[a] The deposition was carried out at –0.63 V (vs Ag/AgCl) for 6 h from a bath containing 0.10 M $CdCl_2$ and 0.15 M TU (pH = 3.25) maintained at 80 °C for all 5 runs.

Five CdS thin films were prepared from a single deposition bath. Table 1 summarizes the passed charge and thickness measured for these films. It is noticed that these values are almost the same for each film, indicating a constant rate of the film growth for each deposition. These CdS films were compared to each other in view of crystallographical and morphological aspects. Figure 1 shows an X-ray diffractogram of a CdS film (Run No. 1 in Table 1). The diffraction peaks other than those from ITO are assigned to hexagonal CdS.[6] The average crystal size of ca. 85 nm was estimated from the full-width half maximum of the (002) diffraction peak by Scherrer's equa-

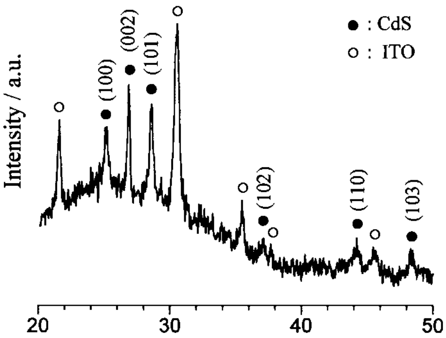

Figure 1. An X-ray diffractogram measured for the CdS thin film deposited from Run 1 in Table 1.

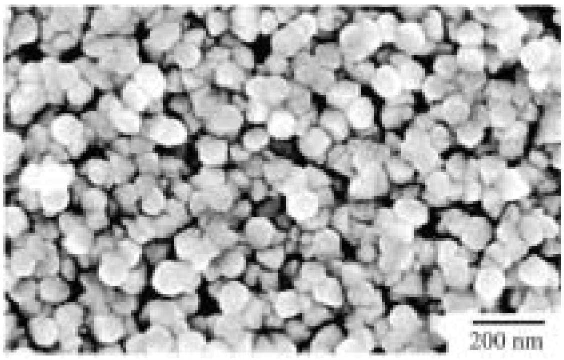

Figure 2. An SEM image of the CdS film deposited from run 1 in Table 1.

tion. An SEM image of the same film is shown in Figure 2. It is clearly seen that the film is made up with hexagonally shaped particles of ca. 85 nm, which is consistent with the size estimated from XRD. Fairly high crystallinity of the deposited film is recognized on considering the film thickness of only 142 nm. Each particle composing the film seems to be made of a single crystal of CdS, as typically expected for the EICD process.[4] The five films deposited from a single bath were indistinguishable for all of these features. Although no further use of the bath was tested, deposition of identical films for higher numbers seemed feasible, because the solution remained clear even after the deposition of five films. This is a remarkable difference from the acidic EICD using TAA we studied earlier, for which the solution became turbid due to homogeneous precipitation of yellowish CdS particles and no recycling of the bath was possible.[4]

Since the formation of fine CdS particles is not visible by eyes, absorption spectra of the deposition bath before and after the electrolyses were measured in order to further check the absence of chemical reactions in the homogeneous phase (Figure 3). The solution shows an absorption peak at 239 nm. The shape and the magnitude of the peak are virtually unchanged after the use. As TU is known to coordinate to Cd^{2+} in aqueous solution (log $\beta_2 = 1.6$),[7] the observed peak is supposed as arising from light absorption of Cd^{2+}–TU complexes. The consumption of this complex by the five-times deposition is too small to expect a detectable change of its concentration. Thus, the unchanged absorption spectra prove the stability of the Cd^{2+}–TU complexes in the acidic bath and rule out the possibility of chemical formation of CdS clusters which should cause an additional absorption

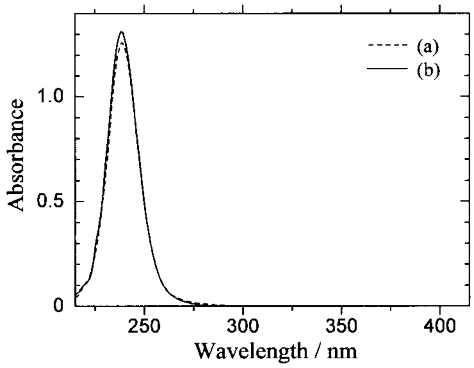

Figure 3. Absorption spectrum of the freshly prepared deposition bath (a) and that after five successive CdS depositions (b). The solutions were diluted thousand times with dilute HCl solution.

in the wavelength between 250 and 450 nm, depending on the size of CdS nanocrystallite.[8,9] Because direct electrochemical reduction of Cd^{2+}–TU complexes was not observed in the cyclic voltammograms measured in aqueous mixtures of Cd^{2+} and TU having various concentrations, the mechanism of the film growth in the present system is expected to be the same as that revealed in the previous study of EICD using TAA, namely, chemical formation of CdS by surface decomposition of Cd^{2+}–TU complexes induced by electrochemical consumption of proton.[4] Studies to elucidate details of the reaction mechanism including kinetics of the film growth are under way.

To our knowledge, EICD from acidic chemical bath containing TU is the best choice for synthesis of highly crystallized CdS thin films. Structural uniformity, high crystallinity and simplicity of the method are the common favorable features of the EICD processes with both TAA and TU. The present system even offers convenience and economical advantage of using just one bath for multiple fabrications of CdS thin films.

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