

Electrodeposition of Nano-Particulate CdS Thin Films in Organic Medium

Tsukasa Yoshida, Kazunori Kondo, Goki Ohta, Koichi Yamaguchi, Takashi Sugiura and Hideki Minoura

Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido 1-1, Gifu 501-1193

Fax: +81-(0)58-293-2587, e-mail: yoshida@apchem.gifu-u.ac.jp

Electrodeposition of CdS thin film from an acetonitrile solution containing $\text{Cd}(\text{ClO}_4)_2$ and thioacetamide has been studied. Although chemical formation of CdS thin film does take place due to precipitation of CdS in the homogeneous solution phase, cathodic electrolysis at the conductive substrate largely enhanced the rate of the film growth. Product analysis by XRD found that both the precipitates and the deposited films consist with nano-size crystallites of CdS. The film growth was apparently linear to the charge consumed with a constant Faradaic efficiency at a given temperature, yet it varied upon varying the reaction temperature between 43 % (40 °C) and 64 % (65 °C). Kinetic analysis of the film growth with and without electrolysis was made by means of electrochemical quartz crystal microbalance (EQCM) under different reaction temperatures. Activation energies of 86.0, 78.6 and 67.5 kJ/mol were determined for the chemical growth of the film, the film growth during electrolysis and the electrochemical reaction at the substrate, respectively. The discrepancy among these values indicates that the film growth during the electrolysis is not under control of the chemical formation of CdS in the bulk of the solution nor the electrochemical process at the substrate, but can be considered as heterogeneous chemical formation of CdS triggered by the electrochemical reaction.

Key Words: cadmium sulfide, thin film, electrodeposition, nano-particles, EQCM

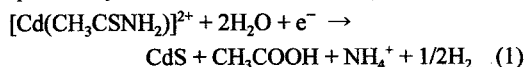
1. INTRODUCTION

Thin film deposition in solutions receives an increasing attention in recent years, because of its practical advantages in lowering cost and environmental stress upon the film processing, as compared to the gas phase techniques such as chemical vapor deposition (CVD) or sputtering. Since the starting materials are present in solvated form, the huge energy to produce gaseous atoms or molecules in the gas phase techniques can be saved [1]. The use of solutions also facilitates the collection and recycling of the waste materials.

Among many kinds of metal sulfides, cadmium sulfide (CdS) is one of the most important materials finding applications in various opto-electronic devices and has been a target of many active studies of chemical [2-5] or electrochemical [4-9] thin film deposition in solutions. While the chemical method, often called as chemical bath deposition (CBD) by analogy to CVD, relies on chemical reactions to precipitate metal sulfides in a thin film form, the electrochemical method, electrodeposition (ED), should achieve the film growth by heterogeneous electrochemical reactions. In order to obtain high quality films with ordered structures, it is necessary to minimize the influence of the chemical reactions in the solution phase to the film growth. With this respect, it is expected that ED offers higher advantages than CBD. However, the hitherto studied ED of CdS thin films from non-aqueous solution dissolving elemental sulfur [6,7] or aqueous solution of thiosulfate

[8] resulted in formation of poorly crystallized random structured films, whereas CBD in alkaline aqueous solution realizes an ordered growth of CdS crystallites, in spite of the formation of many fine CdS particles in the solution phase [2,3]. It is because the film growth is largely dominated by surface reactions in the alkaline CBD, while that by the previous ED methods obviously suffered from the solution phase reactions.

We have recently shown that electroreduction of protons in acidic aqueous chemical bath containing Cd salt and thioacetamide (TAA) realizes a long range atom-by-atom growth of CdS thin films, which is not disturbed by chemical formation of CdS particles in solution [4,5]. Detailed analysis of the growth process revealed that the reduction of protons which were co-produced by hydrolysis of Cd-TAA complex promoted surface catalyzed chemical formation of CdS as expressed by an overall reaction below [5].



It was evidenced that the film growth was not under control of the electrode kinetics. The use of the electrochemical reaction in this system was therefore considered as a control of the surface conditions at the substrate introduced to a CBD process, similarly to the control of the substrate temperature in the CVD process to achieve the film growth only by the surface reactions.

These previous findings prompted us to study electrodeposition of CdS thin films from a Cd salt +

TAA mixture in an aprotic organic solvent. Formation of CdS particles by the hydrolysis of Cd-TAA complex in the solution phase should be prohibited in the organic system. The film growth is therefore to be achieved only by the heterogeneous reactions at the substrate surface.

2. EXPERIMENTAL

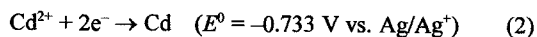
All the chemicals were of commercially available purest grade. Thioacetamide (TAA) was re-crystallized twice in benzene before use. Acetonitrile was distilled twice, subsequently over CaH_4 and P_2O_5 . An indium tin oxide (ITO) coated conductive glass ($10 \Omega/\square$) was used as the substrate, which was cleaned by washing ultrasonically in acetone and 2-propanol.

Electrodeposition and electrochemical measurements were performed in a single compartment cell equipped with three electrodes, the ITO working, a Pt foil counter and a self-made $\text{Ag}/0.01 \text{ M AgNO}_3$ reference electrode. The potential of the Ag/Ag^+ reference was confirmed as +90 mV vs. SCE, by measuring the redox potential of ferrocene/ferricenium ion couple. A mixed solution containing 25 mM $\text{Cd}(\text{ClO}_4)_2$ and 0.1 M TAA in dry acetonitrile served as reaction bath. The film deposition was carried out at -0.8 V vs Ag/Ag^+ and typically at 60°C . Film thickness was measured by a Kosaka SE-2300 surface profilometer. Film growth was also monitored by means of electrochemical quartz crystal microbalance (EQCM), using a Hokuto Denko HQ-101B EQCM controller and a HZ-3000 electrochemical workstation. A vacuum evaporated Au on a 6 MHz AT-cut quartz crystal was used as the electrode in these experiments.

Chemical compositions of the products were analyzed by X-ray photoelectron spectroscopy (XPS) on a Shimadzu ESCA-850. X-ray diffraction (XRD) spectra were obtained by a Rigaku RAD-2R using $\text{CuK}\alpha$ radiation. Surface morphology of the deposited films was observed by a Topcon ABT-150FS scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

The electrochemical reactions in the reaction bath have been studied by cyclic voltammetry (CV) (Fig.1). The CV in a $\text{Cd}(\text{ClO}_4)_2$ solution (a) shows a typical metal plating – anodic stripping behavior, namely, a sharp increase of cathodic current from around -0.9 V due to the reduction of Cd^{2+} to Cd (eq.2) and anodic dissolution of the deposited Cd peaking at around -0.2 V in the reverse scan.



On the other hand, no appreciable reduction current is seen in a solution of TAA (b). It is evident that TAA is not electrochemically reactive in this potential range. When both $\text{Cd}(\text{ClO}_4)_2$ and TAA are present in solution

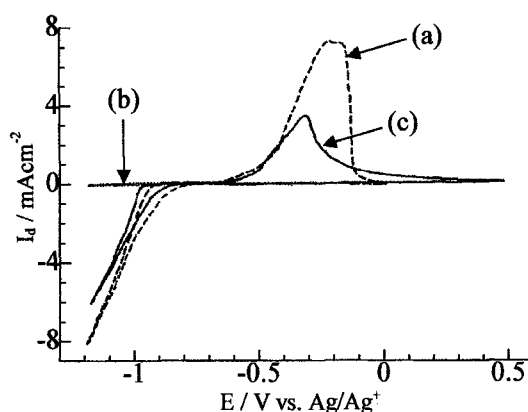
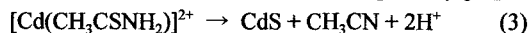


Fig.1 Cyclic voltammograms measured at an ITO electrode in dry acetonitrile solutions containing 25 mM $\text{Cd}(\text{ClO}_4)_2$ (a), 0.1 M TAA (b) and 25 mM $\text{Cd}(\text{ClO}_4)_2$ + 0.1 M TAA (c). Tetrabutylammonium perchlorate was added to all solutions at 0.1 M as supporting electrolyte. The measurements were performed under Ar, at 60°C and at a scan rate of 100 mVs^{-1} .

(c), the onset of the cathodic current for the metallic Cd deposition is shifted negatively by about 0.1 V, as compared to (a). At the same time, the anodic peak of the oxidation of Cd becomes much smaller. The negative shift of the Cd deposition can be reasoned as a consequence of a reduced activity of Cd^{2+} due to its complex formation with TAA. The ratios of the anodic charge over the cathodic charge during the voltammetric scans are 0.83 and 0.57, as found from (a) and (c), respectively. The increased irreversibility in (c) clearly indicates an irreversible cathodic reaction in the mixed solution. Similar voltammetric behavior was observed for the electrodeposition of CdS thin films from an aqueous mixed solution of $\text{CdCl}_2 + \text{NH}_4\text{SCN}$ [9].

Long term electrolysis at -0.8 V , a potential slightly more positive than that for the metallic Cd deposition, in the $\text{Cd}(\text{ClO}_4)_2 + \text{TAA}$ mixed solution resulted in the formation of yellow transparent thin film on the ITO surface. In this attempt was, however, noticed a development of yellow turbidity in the reaction bath. XPS analysis of the deposited thin film and the precipitates collected from the bath found that both of them are composed of CdS, containing a slight excess of Cd ($\text{Cd}:\text{S} = 51.9:48.1$). The chemical formation of CdS from Cd-TAA complex in a dry solvent was unexpected. Although the exact reaction mechanism is yet to be clarified, decomposition of Cd-TAA complex as below can be considered as a possible reaction pathway [10].



Because of the chemical formation of CdS particles in the solution phase, thin films of CdS could be formed on the substrate simply immersed in the reaction bath. Film thickness was measured by surface profilometer for the films deposited under electrolysis at -0.8 V (ED) and under open circuit condition (CBD) for different

reaction times (Fig.2). Film growth is linear to the reaction time elapsed by both ED and CBD. However, only very thin film of 30 nm thickness can be produced by CBD even after 300 min. The growth rate is increased more than 5 times by ED, reaching a thickness of 160 nm after electrolysis for 300 min. It is evident that the film growth is promoted by the electrolysis. A linear relationship was found also between the film thickness and the electric charge consumed during ED. An apparent Faradaic efficiency (η) of 74.6 % (at 60 °C) was determined according to the two-electron reaction as expressed by eq. (4) and by assuming that the density of the film equals to that of bulk CdS (4.58 g/cm³).



XRD spectra of the electrodeposited film and the precipitates formed in the bath are shown in Fig.3. The precipitates show several broad diffraction peaks which can be assigned to CdS. They are probably mixture of cubic and hexagonal CdS, as indicated by the presence of shoulders on both sides of the peak at around $2\theta = 26^\circ$ and a peak at around $2\theta = 47.5^\circ$, which arises from the (103) planes of the hexagonal phase. The

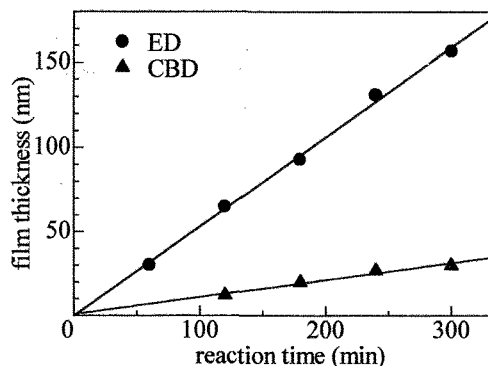


Fig.2 Film thickness plotted versus reaction time for the CdS films deposited by ED at -0.8 V and CBD, at 60 °C.

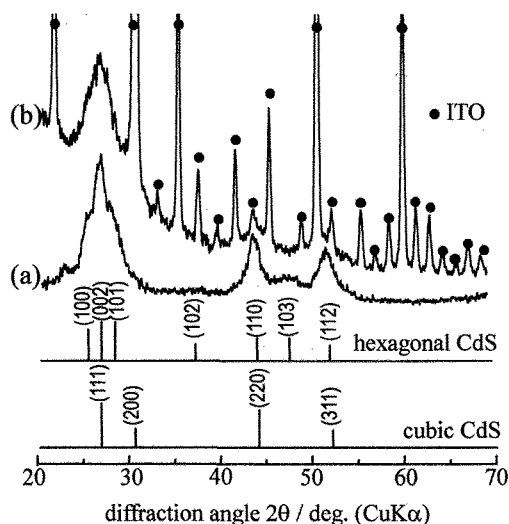


Fig.3 XRD spectra of CdS precipitates formed in the bath (a) and CdS thin film electrodeposited on an ITO at -0.8 V (b). Reaction temperature, time = 65 °C, 180 min.

electrodeposited film, on the other hand, seems to be composed mostly of cubic CdS, as noticed from the symmetrical shape of the peak at $2\theta = 26^\circ$, which is assigned to the diffraction from the (111) planes of the cubic phase. The mean crystal sizes of 4.2 and 6.0 nm were estimated from the full width at half-maximum of the diffraction peaks for the film and the precipitates, respectively. Although highly crystallized CdS thin film was deposited in the relevant aqueous system containing Cd salt and TAA [5], the reaction in the present system was found to yield nano-crystals of CdS both for the film and the precipitates. Electrodeposition from dimethylsulfoxide dissolving elemental S has been also reported to yield nano-crystalline CdS [6], which exhibits quantum size effect [7].

Thin films deposited by CBD and ED were observed by SEM (Fig.4). While the thin film prepared by CBD has a porous structure consisting with spherical particles of 20 to 40 nm in diameter, that by ED is composed of densely packed finer (ca. 20 nm in diameter) particles. The difference in surface morphology also is a clear indication of different growth processes in CBD and ED.

Kinetic analysis has been made for the initial stage of the film growth as well as the electrode process by *in-situ* EQCM. A set of data obtained at 60 °C is shown in Fig.5. Mass change is almost linear to the reaction time both for CBD and ED. Current density during ED is almost constant. Comparison between the thickness data and the mass change from the EQCM data reveals that

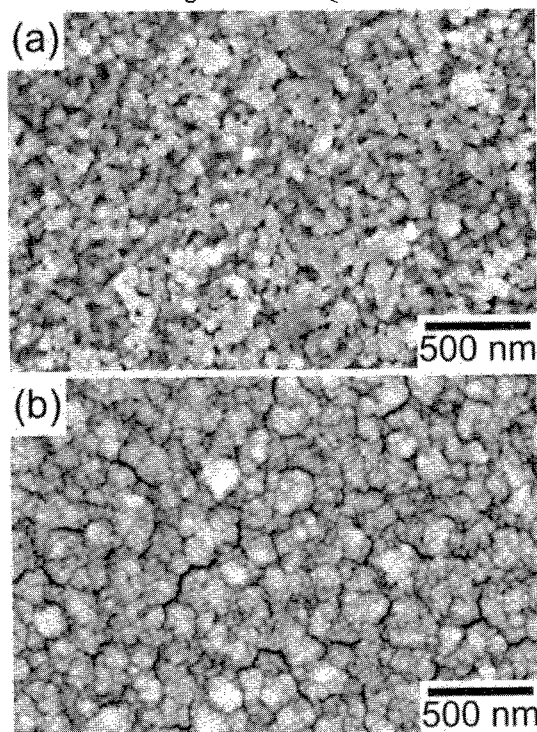


Fig.4 SEM photographs of CdS thin films deposited by CBD (a) and ED at -0.8 V (b). Reaction temperature and time were 65 °C and 180 min, respectively.

the actual density of the electrodeposited CdS film is about 3.9 g/cm³, approximately 15 % smaller than that of the bulk material. Deposition rate is determined from the slope of the mass change in mol/s, while rate of electrochemical reaction is derived by dividing total charge consumed during 10 min by time, being equal to average current density (in A/cm²). The same measurements were performed under various reaction temperatures. Arrhenius plots have been made from the relationship between the reaction temperatures and the reaction rates determined from the EQCM measurements (Fig.6). Activation energies (E_a) for the film growth reactions by CBD and ED, and the electrochemical reaction during ED were calculated to be 86.0, 78.6 and 67.5 kJ/mol, respectively, from the slopes of the Arrhenius plots. It is reasonable to consider that the film growth by CBD is under control of the CdS formation in the solution phase; thus its activation energy being equal to that of the reaction eq. (3). The smaller E_a found for the film growth by ED indicates that it is not under control of the bulk reaction. However, it is also different from the E_a determined from current. If the film growth during electrolysis is a true electrodeposition process, the E_a of the film growth should correspond to that of the electrode process. The difference from typical electrodeposition process is evident also from the temperature dependent change of η determined from the EQCM data (Fig.6). It increases from 43 % to 64 % by increasing the reaction temperature from 40 to 65 °C. This shift of η reflects the difference in E_a . It is therefore evident that the film growth in the present system is not a true Faradaic process, but can be considered as a surface chemical process induced by the electrochemical reaction, similar to the mechanism in the relevant aqueous system [5]. The significant difference is the fact that nano-particulate CdS could be prepared in the present system. Further studies on the properties of the deposited thin films are in progress, giving a main emphasis on the evolution of quantum size effects.

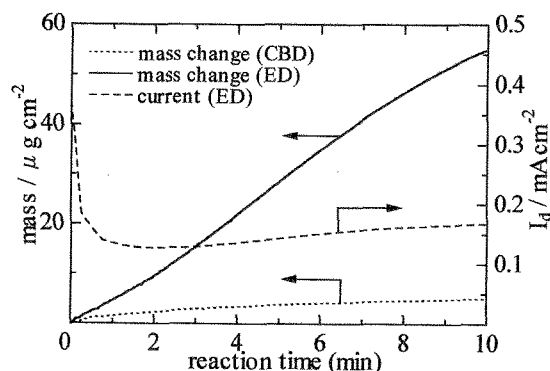


Fig.5 EQCM response showing mass change during CBD and ED at -0.8 V, and current density during the ED. Reaction temperature = 60 °C.

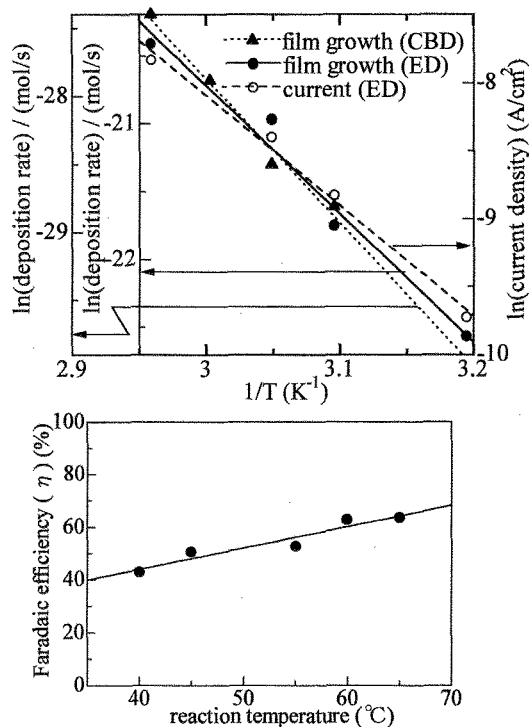


Fig.6 Upper; Arrhenius plots made for the film growth by CBD and ED, and the electrochemical reaction at the substrate. Lower; Variation of Faradaic efficiencies dependent on the reaction temperature, as determined from the EQCM data and assuming the reaction eq. (4).

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