

Cathodic Electrodeposition of Metal Oxide Thin Films from Non-Aqueous Solutions

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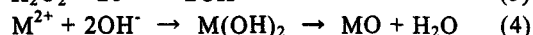
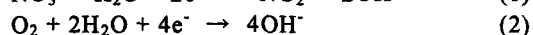
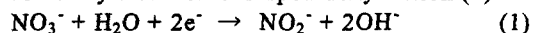
Cathodic electrodeposition of metal oxide thin films has been studied in oxygen saturated dimethyl sulfoxide (DMSO) solution containing Cd(II), In(III) or Sn(IV). Crystalline thin film of CdO can be obtained from DMSO solutions owing to the direct reaction of electrochemically generated super oxide ions with Cd(II) species, while the electrolysis in oxygen saturated aqueous solutions leads to precipitation of Cd(OH)₂. Direct electrodeposition of metal oxides with the same principle has been successful in the case of In(III), for which nano-crystalline In₂O₃ thin films are obtained. However, it does not apply to Sn(IV), for which only metallic Sn films are deposited.

Key words: electrodeposition, non-aqueous solutions, metal oxide, thin film, cyclic voltammetry

1. INTRODUCTION

Fabrication of thin film materials by soft-solution processes such as electrodeposition (ED) and chemical bath deposition (CBD) is very important in view of achieving reduction of cost and environmental stress upon processing.[1] Although the solution processes were often considered to yield materials in poorly controlled structures, recent examples of epitaxial thin film growth, such as CBD of CdS on InP(111), [2] ED of Cu₂O on Au(100), [3] and ED of ZnO on GaN(002) [4] have proven that the solution phase processing does realize the synthesis of high quality materials.

Cathodic electrodeposition of metal oxide thin films from aqueous solutions is generally considered to proceed according to the following scheme; OH⁻ ions are generated by electrochemical reduction of nitrate (1), dissolved molecular oxygen (2) or hydrogen peroxide (3), which subsequently react with metal ions to precipitate corresponding metal hydroxides and eventually metal oxides upon dehydration (4).



Electrodeposition of metal oxide thin films according to the above-mentioned processes have been successfully carried out in case of ZnO.[5-7] However, ZnO in fact is the almost only material that results in the direct crystallization of metal oxide. In most other cases such as TiO₂ [8] and ZrO₂ [9], the electrodeposition yields only hydroxide films which have to be heated for crystallization. Since the formation of hydroxide species cannot be avoided in protic solvents, direct synthesis in water is possible only for a limited number of metal oxides.

Unlike the aqueous systems, electrodeposition

from non-aqueous solutions is less explored and thus offers various possibilities for new synthesis. Cathodic electrodeposition of crystalline ZnO thin films has been reported from aprotic solutions of propylene carbonate containing nitrate [10] and dimethyl sulfoxide (DMSO) saturated with oxygen.[11] However, the principle of oxide formation is not well understood in these systems. It is also unknown whether such processes can be applied to various metal oxides else than ZnO. In this study, we have attempted cathodic electrodeposition of oxide thin films from oxygen saturated DMSO solutions for Cd(II), In(III) and Sn(IV), which belong to the group IIB, IIIB and IVB elements, respectively. The mechanism of oxide formation in the aprotic system and the limitation in its versatility are discussed.

2. EXPERIMENTAL

Cadmium chloride 2.5 hydrate (CdCl₂·2.5H₂O), cadmium perchlorate hexahydrate (Cd(ClO₄)₂·6H₂O), indium chloride anhydrous (InCl₃) and tin chloride pentahydrate (SnCl₄·5H₂O) were of analytical reagent grade and used as received. Dimethyl sulfoxide (boiling point = 189°C) was dried with molecular sieve (3 Å) before use. Indium tin oxide (ITO) coated conductive glass (10 Ω/sq.) was used as the substrate in case of the Cd(II) and Sn(IV) systems, while F-doped tin oxide (FTO) (20 Ω/sq.) glass was used for the In(III) system.

All the studies by cyclic voltammetry and electrodeposition were performed in a single compartment cell with three electrodes, the substrate as a working, a Pt foil as a counter and a saturated calomel electrode (SCE) for aqueous system or a home-made Ag/Ag⁺ (-0.05 V vs. SCE) electrode for non-aqueous system as a reference. All the potentials noted hereafter are

corrected with respect to SCE. The deposition baths were 5 mM $\text{CdCl}_2 + 0.1 \text{ M KCl}$ in water, 5 mM $\text{Cd}(\text{ClO}_4)_2 + 0.1 \text{ M LiClO}_4$ in DMSO, 0.1 M $\text{InCl}_3 + 0.1 \text{ M LiCl}$ in DMSO and 0.1 M $\text{SnCl}_4 + 0.1 \text{ M LiCl}$ in DMSO. They were saturated either with Ar or O_2 . The temperature was maintained at 70°C for the aqueous solution [6] in a water bath and 150°C for the DMSO solution [11] in an oil bath, according to the conditions used in the precedent studies. Film deposition was carried out by potentiostatic electrolysis in the potential range between -0.5 and -1.1 V for 30 min.

X-ray diffraction (XRD) patterns of the deposited films were measured on a Rigaku RAD-2R using $\text{Cu K}\alpha$ radiation. Surface morphology and the fine structure of the films were observed by a Topcon ABT-150FS scanning electron microscope (SEM) and a Hitachi H-8000 transmission electron microscope (TEM), respectively. The UV-Vis absorption spectrum was measured in diffuse reflection on a Hitachi U-4000 spectrophotometer.

3. RESULT AND DISCUSSION

As mentioned in the introduction, crystalline thin films of ZnO can be electrodeposited from aqueous solutions of Zn salt.[5-7] Similar electrochemical behavior can be expected for Cd because it also belongs to the same group IIB elements in the periodic table. Cathodic reaction in an aqueous solution of CdCl_2 has been therefore studied in the presence and absence of O_2 by means of cyclic voltammetry (Fig. 1). Increase of cathodic current along the cathodic scan and anodic peak on reversal of the potential sweep are detected under Ar, which are typically assigned to the deposition of metallic Cd and anodic stripping of the electrode, respectively. Although the overall character of the voltammogram in the presence of O_2 is similar to that under Ar, an increase of cathodic current is noticed in the potential range between -0.4 and -0.8 V , which presumably arise from irreversible reduction of O_2 . Decrease of anodic peak is also noticed, in spite of the almost unchanged

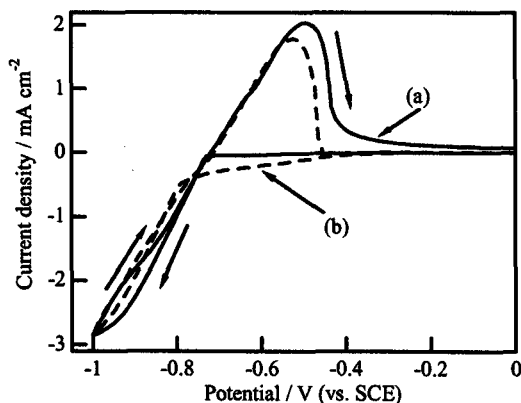


Fig. 1 Cyclic voltammograms measured at an ITO coated glass electrode in an aqueous solution containing 5 mM CdCl_2 and 0.1 M KCl , saturated with Ar (a) or O_2 (b). Temperature = 70°C , Scan rate = 100 mV s^{-1} .

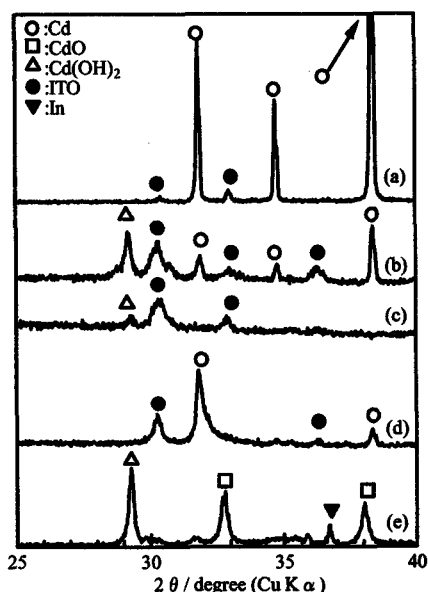
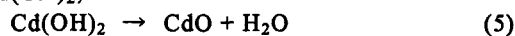


Fig. 2 XRD patterns of the thin films electrodeposited on ITO coated glass substrates from an aqueous solution (70°C) containing 5 mM CdCl_2 and 0.1 M KCl at -0.9 V under Ar (a), at -0.9 V under O_2 (b) and at -0.7 V under O_2 (c); those electrodeposited at -1.1 V from a DMSO solution (150°C) containing 5 mM $\text{Cd}(\text{ClO}_4)_2$ and 0.1 M LiClO_4 under Ar (d) and O_2 (e).

magnitude of the cathodic current related to Cd deposition. When the reversibility of the reaction is estimated from the ratio of the total anodic charge over the total cathodic charge in the voltammograms, it drops from 0.95 (Ar) to 0.52 (O_2). These results imply precipitation of Cd hydroxide or oxide triggered by the irreversible reduction of O_2 , although the presence of O_2 is not blocking the deposition of metallic Cd, unlike the case with Zn.[12]

Potentiostatic electrolysis has therefore been performed at -0.7 or -0.9 V and under Ar or O_2 . The XRD patterns of the product films are shown in Fig. 2. Under Ar and at -0.9 V , diffraction peaks assigned to metallic Cd are only observed besides those arising from the substrate, thus confirming the deposition of a Cd film. Under O_2 at -0.9 V , a mixture of $\text{Cd}(\text{OH})_2$ and Cd is obtained. At -0.7 V , the potential more positive than that for the deposition of metallic Cd, a colorless translucent film is deposited under O_2 , which indicate the diffraction peak of $\text{Cd}(\text{OH})_2$. Formation of CdO was not observed in all cases. It is therefore concluded that the hydroxide formation promoted by the electroreduction of O_2 does operate in an aqueous solution of CdCl_2 , but its subsequent conversion to CdO does not take place. The difference from Zn can be reasoned on considering the positive value of Gibbs free energy ($\Delta G = 8.0 \text{ kJ mol}^{-1}$) for the dehydration of $\text{Cd}(\text{OH})_2$,



which is calculated from the Gibbs free energy of formation (ΔG_f°) of each chemical species in eq. 5.[13] Corresponding ΔG value for the formation of ZnO is slightly negative (-1.8 kJ mol^{-1}) and

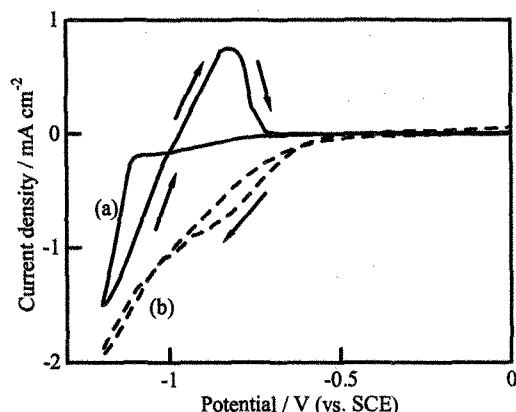


Fig. 3 Cyclic voltammograms measured at an ITO coated glass electrode in a DMSO solution containing 5 mM $\text{Cd}(\text{ClO}_4)_2$ and 0.1 M LiClO_4 , saturated with Ar (a) or O_2 (b). Temperature = 150°C , Scan rate = 100 mV s^{-1} .

thus spontaneous dehydration of $\text{Zn}(\text{OH})_2$ can be expected.

In the next step, we have tried to electrodeposit oxide thin films from an oxygen saturated DMSO solution containing $\text{Cd}(\text{ClO}_4)_2$, in which formation of OH^- can be avoided. Cyclic voltammograms measured under Ar and O_2 are shown in Fig. 3. Typical reversible behavior of metallic Cd deposition similar to that in the aqueous system is seen under Ar. In the presence of O_2 , a large enhancement of cathodic current occurs in the potential range negative than -0.7 V . At the same time, the anodic peak associated with the oxidation of Cd completely disappears. Similar irreversible behavior was reported in the case of ZnO electrodeposition performed in the equivalent system.[11] Possibilities for the electrodeposition of CdO is therefore strongly suggested in the DMSO solution.

Potentiostatic electrolysis at -1.1 V in fact resulted in a formation of brownish film under O_2 , while that under Ar yields a grayish film. However, the brown film deposited under O_2 gradually turned its color into white on its exposure to air. The color change could be suppressed when the film was stored in a desiccator. XRD patterns of such stored films are shown in Fig. 2. The gray film indicates diffractions of metallic Cd, whereas the brown film deposited under O_2 shows the presence of both CdO and $\text{Cd}(\text{OH})_2$. It is supposed that the change of the color is associated with the hydration of CdO to $\text{Cd}(\text{OH})_2$ by the moisture in air, according to the reversal of eq. 5, which can be spontaneous due to its negative ΔG .

Formation of CdO has also been supported from the absorption spectrum of the brown film, which lead to a determination of a bandgap energy of direct transition as 2.49 eV , being close to the literature value of CdO (2.5 eV).[14] Difference between the products obtained under O_2 and Ar is also obvious from their morphologies (Fig. 4). The film deposited under O_2 consists of large grains of 3 to $6 \mu\text{m}$ size, while much smaller (ca. $0.2 \mu\text{m}$) particles are

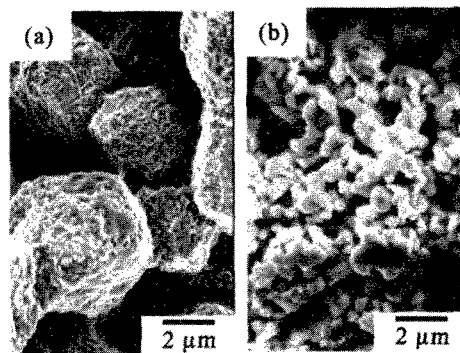
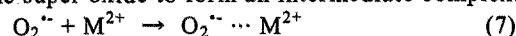


Fig. 4 SEM photographs of the thin films electrodeposited at -1.1 V on ITO coated glass substrates from a DMSO solution (150°C) containing 5 mM $\text{Cd}(\text{ClO}_4)_2$ and 0.1 M LiClO_4 under O_2 (a) and Ar (b).

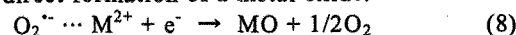
found for that under Ar. It is also noticed that the surface of the particles deposited under O_2 is not smooth, although they are angularly shaped as a whole. It is supposed that the surface roughness is caused by the hydration of CdO to $\text{Cd}(\text{OH})_2$. Although preparation of pure CdO film was not possible due to its poor stability in moist air, the present results have proven that direct electrodeposition of crystalline CdO is indeed possible in an aprotic solvent like DMSO. In aqueous systems, electroreduction of O_2 results in a formation of OH^- ions as the electrophilic protons readily react with anion radicals of oxygen. The precipitation of metal oxide therefore can proceed only via the hydroxide route expressed in eq. 4. This should also be the case for nitrate and hydrogen peroxide precursors. In aprotic systems, however, it is known that reduction of O_2 results in a formation of super oxide ion ($\text{O}_2^{\cdot-}$).[15]



In such media, the added metal cations are the most electrophilic species and thus interact with the super oxide to form an intermediate complex.



Further reduction of this complex would result in a direct formation of a metal oxide.



In the final step, we have examined how far we can extend the above mentioned principle by attempting electrodeposition of In_2O_3 and SnO_2 thin films. Cyclic voltammograms measured in a DMSO solution containing InCl_3 in the presence and absence of O_2 indicated very similar behaviors as those seen for the CdCl_2 system, namely, a large enhancement of cathodic current below -1.1 V and blocking of metallic In deposition under O_2 (figure not shown). Potentiostatic electrolysis at -1.6 V has yielded a white film under O_2 , which, however, does not exhibit any XRD peaks aside from those of the substrate (Fig. 5). When the film is fired at 350°C for 30 min under N_2 , crystallization of In_2O_3 is confirmed from XRD. In order to confirm further the formation of In_2O_3 , the as-deposited film has been scratched off the substrate and observed by

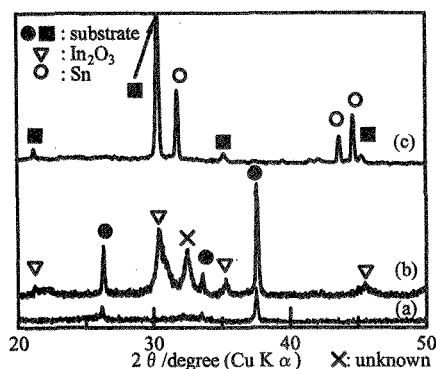


Fig. 5 XRD patterns of the thin film as-electrodeposited at -1.6 V on an FTO coated glass substrate from a DMSO solution (150°C) containing 0.1 M InCl_3 and 0.1 M LiCl under O_2 (a) and the same film fired at 350°C for 30 min under N_2 (b); that electrodeposited at -1.6 V on an ITO coated glass substrate from a DMSO solution (150°C) containing 0.1 M SnCl_4 and 0.1 M LiCl under O_2 (c).

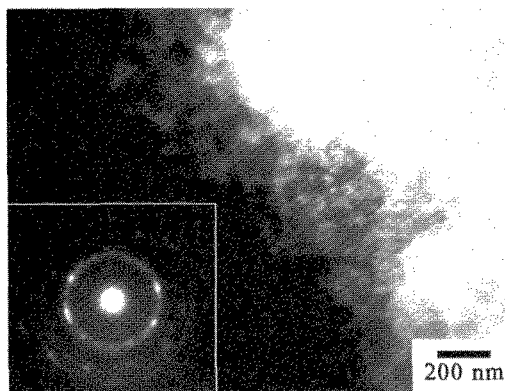


Fig. 6 TEM photograph of the specimen prepared by scratching off the film same as that of Fig. 5(a) and its SAED pattern (inset).

TEM (Fig. 6). It can be seen that the electrodeposited film consists of nano-sized particles of about 30 nm. The selected area electron beam diffraction (SAED) of this sample shows several rings which are assigned to In_2O_3 . Although not highly crystallized, direct formation of In_2O_3 has therefore been proven by electrodeposition from a DMSO solution.

Electrodeposition of SnO_2 , however, was not possible from DMSO solutions containing SnCl_4 , despite of the fact that increase of cathodic current due to O_2 reduction was observed in cyclic voltammograms (figure not shown). Potentiostatic electrolysis has been conducted at various potentials, but resulted only in a formation of metallic Sn films regardless of the atmosphere (Fig. 5). Deposition of lower oxides such as SnO was also not detected. Since formation of oxides of group IVB metals requires multi electron transfer in the reaction subsequent to the formation of intermediates as expressed for the group IIB metal by eq. 8, direct formation of metal oxide may become difficult. Although the electrodeposition has been carried out at 150°C one might also consider the effect of residual

water which is introduced as crystal water of SnCl_4 . Further studies with controlled water content and of other tetravalent metal cations such as Ti(IV) and Zr(IV) are under way in order to gain more information to complete the present discussion.

4. CONCLUSION

It has been found that cathodic electrolysis in oxygen saturated aqueous solution of CdCl_2 only yields a Cd(OH)_2 thin film as its dehydration to CdO does not take place spontaneously from thermodynamic viewpoint. By contrast, crystalline CdO thin films can be electrodeposited from DMSO solution owing to the direct reaction of electrochemically generated $\text{O}_2^{\cdot-}$ with Cd(II) species, although the deposited CdO is unstable in moist air. The same principle seems to be operative for the oxide formation of the group IIIB metals such as In(III) but not for the group IVB metals such as Sn(IV) .

ACKNOWLEDGMENT

The present study was partly defrayed by the Industrial Technology Research Grant Program in '02 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan (01B64002c).

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