Preparation of thin films of MnO$_2$ and CeO$_2$ by a modified chemical bath (oxidative-soak-coating) method

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Thin films of MnO$_2$ and CeO$_2$ were deposited on glass substrates directly from aqueous solutions in a temperature range from 313 to 333 K by a modified chemical bath deposition technique. The principle of the film deposition was based on the oxidation of Mn^{2+} and Ce^{3+} ions in homogeneous solutions and subsequent heterogeneous nucleation of MnO$_2$ and CeO$_2$ on the substrates. We have named this method as "oxidative-soak-coating" method. The film thicknesses after a 24-hour deposition were 1 μm and 60 nm, respectively. Thin films consisting of Mn$_3$O$_4$ and MnOOH were also deposited by changing the pH of the starting solutions for the deposition of MnO$_2$. The effects of the composition of the starting solution, deposition temperature, and the compatibility of the substrates to the film substances were investigated. © *2003 Kluwer Academic Publishers*

1. Introduction

Since manganese oxides (MnO$_x$) have unique electrical and chemical properties, thin films of MnO$_x$ can be used for the electrode material of capacitors [1, 2], electrochromic devices [3, 4], ion-exchangers [5], and selective adsorption material of radionuclides [6]. Also, cerium dioxide (CeO$_2$) thin films are known to have important applications as buffer layers for high temperature perovskite superconductors, corrosion-resistant coatings, photocatalysts, UV absorbers, electrochromic devices, or electrodes for solid oxide fuel cells (SOFC). For the preparation of MnO$_x$ thin films, sol-gel methods [1, 2, 4, 5] and anodic oxidation of Mn^{2+} [1–3] ion have been widely used, and for CeO$_2$ thin films, numerous methods such as CVD [7], RF sputtering [8], sol-gel [9–12], or spray pyrolysis [13, 14] have been reported.

Direct deposition of oxide thin films from aqueous solutions, which has been extensively reviewed by Niesen and De Guire [15], has advantages over above-mentioned techniques because it enables us to prepare oxide thin films on non-conducting, less refractory substrates. When one wishes to deposit oxide thin films on pores in porous substrates, for example, direct deposition techniques should be especially advantageous. The principles of the direct deposition of oxide thin films from aqueous solutions are based on a gradual increase in supersaturation of metal ions by means of spontaneous hydrolysis of soluble precursors [16–20] or oxidation of metal ions [21–23] so that heterogeneous nucleation of films becomes more predominant than homogeneous nucleation. Various oxide thin films such as ZnO, SnO$_2$, TiO$_2$, Fe$_3$O$_4$, SiO$_2$ or CeO$_2$ have been prepared through the direct deposition techniques.

It is a general tendency that ions with higher oxidation state (eg. Sn^{4+}) are more prone to undergo hydrolysis to precipitate as (hydr) oxides (eg. SnO$_2$) than the same ions with lower oxidation state (eg. Sn^{2+}). Therefore, a gradual oxidation of ions is a promising strategy to obtaining oxide thin films via heterogeneous nucleation. As far as the oxidation-based technique is concerned, a name "ferrite plating" has been given to the method for the deposition of ferrite films [21, 22]. According to Niesen and De Guire [15], the ferrite plating is categorized in the chemical bath deposition technique. However, the oxidation-based technique shall be applicable to other systems than ferrites. We therefore would like to name the oxidation-based, chemical bath deposition of oxide thin films in general as "oxidative-soak-coating" method [24].

Mindt [23] deposited MnO$_2$ thin films by oxidizing Mn^{2+} ion with persulfate ion (S$_2$O$_8^{2-}$) at room temperature. By this method, however, the oxidation of Mn^{2+} takes place so fast that a powdery precipitate of MnO$_2$ comes out to a large extent. Izaki *et al.* [25] have prepared CeO$_2$ thin films by raising the pH of Ce^{3+}-containing solutions using reduction of nitrate ion with dimethylaminoborane (DMAB), followed by spontaneous hydrolysis and oxidation of Ce^{3+}.

In the present work, MnO$_2$ and CeO$_2$ thin films were directly prepared from homogeneous aqueous solutions containing Mn^{2+} or Ce^{3+} ions at temperatures from 313 to 333 K by the oxidative-soak-coating method. Factors
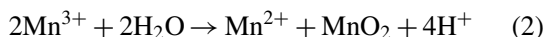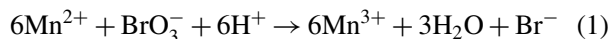
affecting the film formation and film quality as well as the polymorphs of manganese oxides were investigated.

2. Experimental procedure
2.1. Preparation of MnO_2 thin films
Manganese(II) chloride tetra hydrate, $MnCl_2 \cdot 4H_2O$, and sodium bromate, $NaBrO_3$, of analytical grade purities were dissolved in deionized water in 0.1 dm^3 beakers at room temperature. The concentrations of $MnCl_2 \cdot 4H_2O$ and $NaBrO_3$ were adjusted in the ranges of 0.005 to 0.02 mol/dm^3 and 0.01 to 0.2 mol/dm^3, respectively. The pH values of as-prepared solutions were in the range from 4.8 to 5.3, depending on the solute concentration. In some cases, pH of the solutions was raised to about 7.5 by adding appropriate amounts of sodium acetate, CH_3COONa. Glass slides were immersed in the solutions, and the solutions were left to stand at temperatures between 323 and 343 K for 24 hours. The top of the beakers were covered with watch glasses to suppress the loss of the solutions due to evaporation. In some cases, the surfaces of the glass substrates had been coated with TiO_2 to see the effect of the surface substance on the film deposition. For the TiO_2 coating, glass slides were dip-coated with a commercial titania sol ($TPX^{®}$ Sadec Co. Ltd., Japan) and heat-treated in air at 773 K for 10 minutes.

The chemical reactions that are expected to occur in the solutions are the oxidation of Mn^{2+} to Mn^{3+} (1), and disproportionation of Mn^{3+} to Mn^{2+} and MnO_2 (2).

$$6Mn^{2+} + BrO_3^- + 6H^+ \rightarrow 6Mn^{3+} + 3H_2O + Br^- \quad (1)$$

$$2Mn^{3+} + 2H_2O \rightarrow Mn^{2+} + MnO_2 + 4H^+ \quad (2)$$

When the rate of reaction (1) is slow enough for heterogeneous nucleation to predominate, nucleation of MnO_2 would occur on the interfaces between the solution and immersed substrates or inner wall of the beaker, then thin film deposition can be expected. Under optimum conditions as described below, dark gray-colored thin films were deposited.

2.2. Preparation of CeO_2 thin films
Cerium(III) acetate, $Ce(CH_3COO)_3$, and potassium chlorate, $KClO_3$, of analytical grade purities were dissolved in deionized water. The concentration of $Ce(CH_3COO)_3$ was fixed to 0.01 mol/dm^3, while the concentration of $KClO_3$ was varied from 0.01 to 0.1 mol/dm^3. Fused silica slides were immersed in the solutions, and the solutions were left to stand at temperatures between 303 and 333 K, in a similar manner to the MnO_2 system. Fused silica slides were used for the characterization of UV-VIS transmittance of the films as described later. The chemical reactions that are expected to occur are the oxidation of Ce^{3+} to Ce^{4+} (3), and spontaneous hydrolysis of Ce^{4+} (4).

$$2Ce^{3+} + ClO_3^- \longrightarrow 2Ce^{4+} + ClO_2^- \quad (3)$$

$$Ce^{4+} + 2H_2O \longrightarrow CeO_2 + 4H^+ \quad (4)$$

Reaction (3), however, is disputable because the standard redox potential of the Ce^{3+}/Ce^{4+} pair (1.74 V vs.

NHE, 298 K) is higher than those of the ClO_3^-/ClO_2^- pair (1.21 V) or the ClO_2^-/ClO^- pair (1.645 V), meaning that ClO_3^- is not likely to oxidize Ce^{3+} at 298 K. As will be described later, however, the deposition of CeO_2 thin films did take place at temperatures higher than 313 K. Therefore, we speculate that ClO_2^-, which had existed as an impurity or had been formed by the decomposition of ClO_3^-, might be responsible for the oxidation of Ce^{3+} at elevated temperatures. The true mechanism of the oxidation of Ce^{3+} is still unclear, though.

2.3. Characterization of films
The resultant MnO_2 and CeO_2 thin films were characterized for crystalline phases by X-ray diffraction (XRD, Model XD-D1, Shimadzu, Japan), film thickness with a surface profilometer (Model Dektak3030, ULVAC, Japan), microstructure with a scanning electron microscope (SEM, Model JSM-T330A, JEOL, Japan), and for CeO_2 thin films, UV-VIS transmittance with a spectrophotometer (Model U-3000, Hitachi, Japan).

3. Results and discussion
3.1. MnO_2 thin films
Table I shows the effect of the composition of the starting solution on the film formation at 333 K. The optimum concentration range of Mn^{2+} ion was quite narrow, around 0.01 mol/dm^3; when it was 0.005 mol/dm^3, no precipitate came out, and when it was 0.02 mol/dm^3, homogeneous nucleation became pronounced and the surfaces of the films became rough due to the adhesion

TABLE I Effect of the composition of the starting solution on film formation of MnO_2 on uncoated glass at 333 K.

	Mn^{2+} (mol/dm^3)		
	0.005	0.01	0.02
BrO_3^- (mol/dm^3)			
0.01	X	X	X
0.05	X	A	B
0.1	X	A	B
0.2	X	A	B

X: No or extremely slow film formation.
A: Film formation with very small amounts of powdery precipitate.
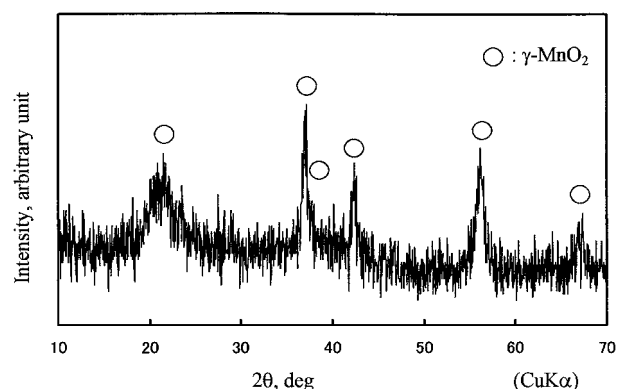B: Film formation with large amounts of powdery precipitate.

Figure 1 X-ray diffraction pattern of a manganese oxide thin film deposited from a solution of which initial pH was 5.0.

of powdery precipitates. The optimum temperature for the film deposition was 333 K; at 323 K, the deposition rate was very slow, and at 343 K, the surfaces of the films became rough due to the predominant homogeneous precipitation as mentioned above. So a standard composition of the starting solution was set as follows; $MnCl_2 \cdot 4H_2O$: 0.01 mol/dm^3, and $KBrO_3$: 0.1 mol/dm^3. Under this condition, films were formed both on the substrate and on the inner walls of the beakers. It seems that the ratio of BrO_3^- to Mn^{2+} should be in excess with respect to the stoichiometry. Otherwise, the rate of the film deposition slows down with a consumption of BrO_3^-.

The TiO_2 coating on the glass substrates promoted heterogeneous nucleation to a large extent and it improved the ease and reproducibility of film formation. When TiO_2-coated substrates were used, therefore, high quality films were obtained in shorter deposition
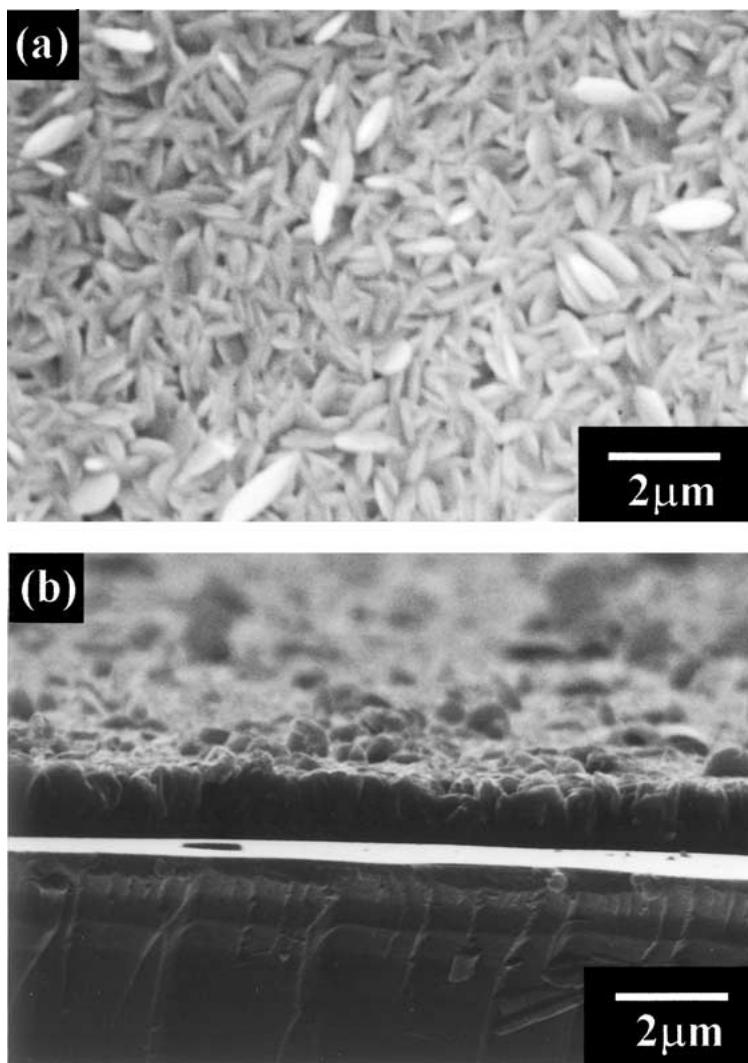

Figure 2 Scanning electron micrographs of the (a) surface and (b) cross-section of a γ-MnO$_2$ thin film.
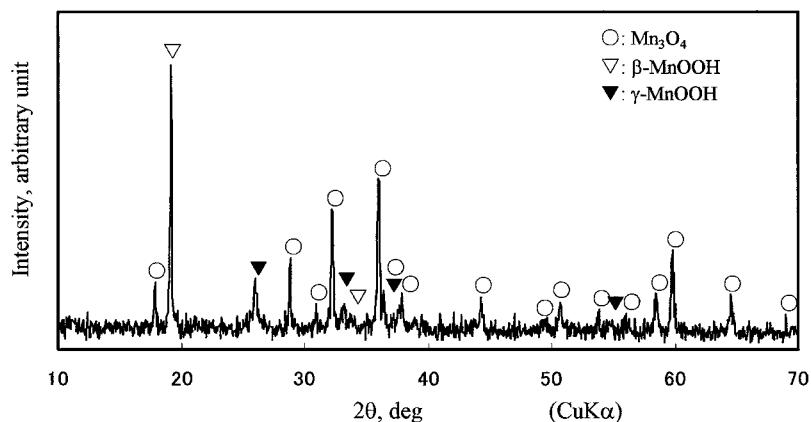

Figure 3 X-ray diffraction pattern of a manganese oxide thin film deposited from a solution of which initial pH was 7.5.

time or from solutions having lower solute concentrations. The initial pH of the starting solution was around 5.0, and it decreased to around 2.0 after a 24-hour deposition because protons were liberated accompanied with the formation of MnO_2 (Equation 2).

Fig. 1 shows the X-ray diffraction profile of the film deposited from a starting solution of pH 5.0. The substance was identified to be γ-MnO_2 (Nsitite). Although there are a number of polymorphs of MnO_2, γ-MnO_2 is most commonly found in chemical precipitates made at room temperature. It has been established that γ-MnO_2 is not a stoichiometric phase and that it contains small amounts of Mn^{2+}, Mn^{3+} and OH^- [26]. Fig. 2 shows the surface and cross-section micrographs of a γ-MnO_2
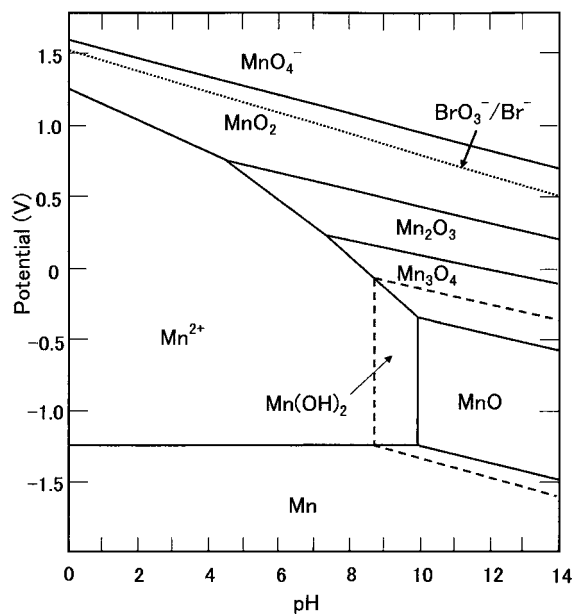

Figure 4 The pH-potential diagram for Mn (0.01 mol/dm^3) - H_2O system.

thin film. The film consisted of tightly packed fusiform particles. These particles, however, should not be single crystals but agglomerates of much smaller crystals because XRD peaks in Fig. 1 are quite broad. The film thickness after a 24-hour deposition was about 1 μm.

When the initial pH of the starting solution was adjusted to 7.5, brown-colored thin films were obtained. The optimum composition range was also narrow; a typical composition was 0.005 mol/dm^3 of $MnCl_2 \cdot 4H_2O$, 0.01 mol/dm^3 of $NaBrO_3$, and 0.2 mol/dm^3 of CH_3COONa. The films were mixtures of Mn_3O_4, β-$MnOOH$, and γ-$MnOOH$ as shown in Fig. 3, and the film thickness after a 24-hour deposition was about 400 nm. After a 24-hour deposition at 333 K, the pH shifted to 7.0.

The variation of the crystalline phase may be explained by the pH-potential diagram as shown in Fig. 4. Fig. 4 can be unequivocally drawn by using the data of standard redox potentials and Nernst's equation. When the pH of the solution lies in a region from 5.0 to 2.0 during the film deposition, the predominant phase to precipitate should be MnO_2. In the present case, γ-MnO_2 was precipitated. On the other hand, when the pH of the solution lies in a region from 7.5 to 7.0, the precipitating phases should be Mn_3O_4 and Mn_2O_3. Assuming that Mn^{3+} in aqueous media might appear as hydrolyzed phases like β- and γ-$MnOOH$, the experimental results are consistent with Fig. 4.

3.2. CeO_2 thin films

Transparent CeO_2 thin films were obtained when the deposition temperature was set in a range from 313 to 323 K from all the solutions. When the deposition temperature was 333 K, however, the adhesion to the substrates was so poor that the films were easily washed off upon rinsing with water. When $KClO_3$ content was
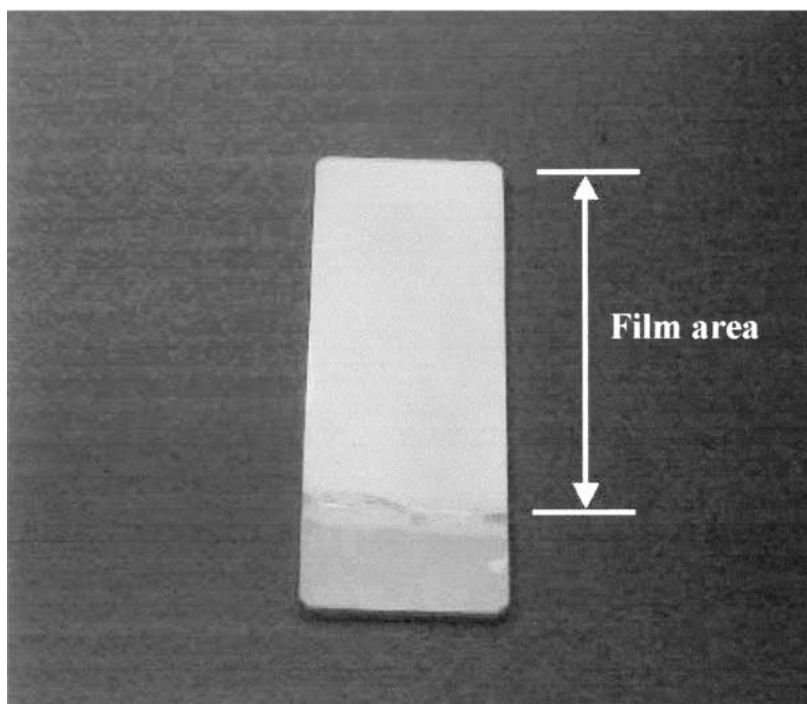

Figure 5 Picture of a CeO_2 thin film. Reflected light indicates the film area.
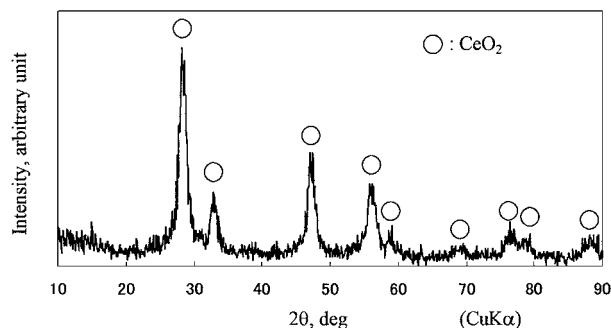
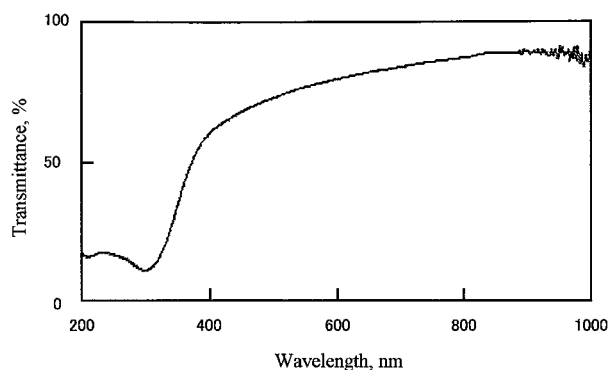*Figure 6* X-ray diffraction pattern of a thin film of CeO_2.

Figure 7 UV-VIS transmittance spectrum of a CeO_2 thin film deposited on a fused silica substrate. The absorption of the substance has been subtracted.

high, 0.1 mol/dm^3, powdery precipitate came out as well and the resultant films became turbid. Fig. 5 shows a picture of an as-deposited thin film. In the picture, reflected light indicates the area on which the thin film is deposited. The film thickness after a 24-hour deposition was about 60 nm. Fig. 6 shows the XRD profile of the film substance deposited at 333 K and scraped from the substrates. It was identified to be CeO_2. Fig. 7 shows a UV-VIS transmittance spectrum, indicating the UV-absorbing property characteristic to CeO_2.

We made some efforts to increase the film thickness by elongating the deposition time or by repeating the film deposition successively. However, those attempts resulted in the peel-off of the films from the substrates even though a single 24-hour deposition gives excellent thin films. TiO_2 coating on the substrate was effective to avoid the peeling off, while SiO_2 or Al_2O_3 coatings were not. Although we have not been able to give a quantitative explanation, the improvement of the compatibility of the substrate to CeO_2 should be a key to obtaining thicker films.

4. Summary

γ-MnO_2 thin films of about 1 μm in thickness were deposited on glass substrates from simple solutions containing Mn^{2+} and BrO_3^- at 333 K. By raising the pH of the starting solutions to 7.5, thin films consisting of Mn_3O_4, β-$MnOOH$, and γ-$MnOOH$ were also obtained. Visually transparent CeO_2 thin films of about 60nm in thickness were deposited on fused silica substrates from solutions containing Ce^{3+} and ClO_3^- at 313 and 323 K. For both films, the control of the composi-

tion of the starting solution and the deposition temperature was important. Since the present technique makes use of heterogeneous nucleation of the film substances on the substrates, the compatibility of the substrate to the film substance considerably affects the ease and reproducibility of the film formation.

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