

Novel Sol-Gel Technique for Preparing Single-Phase Complex Oxide Thin Films from Aqueous Solutions of Metal Salts

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The paper presents aqueous solution-based sol-gel deposition technique for complex oxide coatings. Coating solutions were prepared by dissolving the corresponding metal salts and polyvinylpyrrolidone (PVP) in water, where the solutions did not contain alcohols, where are usually used in conventional alkoxide-based sol-gel technique. Dip- or spin-coating was conducted on SiO₂ glass or single-crystal Si substrates, followed by firing, with or without cycling the gel film deposition and firing. NiFe₂O₄, Y₃Fe₅O₁₂, LaCoO₃ and BaTiO₃ thin films were prepared, respectively, from Ni(CH₃COO)₂·4H₂O - Fe(NO₃)₃·9H₂O - PVP - H₂O, Y(NO₃)₃·6H₂O - Fe(NO₃)₃·9H₂O - PVP - H₂O, La(NO₃)₃·6H₂O - Co(NO₃)₂·6H₂O - PVP - H₂O and Ba(CH₃COO)₂ - (CH₃CH(O-)NH₄)₂Ti(OH)₂ - PVP - H₂O solutions. The fired films obtained were 0.05-0.5 μm in thickness, depending on the number of the deposition cycles, solution viscosity, and heat-treatment conditions, and were all single-phase in corresponding complex oxides as was revealed in X-ray diffraction patterns. Macroscopic cracks were not detected by the naked-eye or optical microscopic observation, while some of the films showed microscopic cracks in SEM images when deposited on SiO₂ glass substrates. Such microscopic cracks, however, did not form when the films were deposited on single-crystal Si substrates, which have larger thermal expansion coefficient than SiO₂ glass.

Key words: Complex oxide, Coating films, Aqueous solution, NiFe₂O₄, Y₃Fe₅O₁₂, LaCoO₃, BaTiO₃

1. INTRODUCTION

Alkoxide-based sol-gel thin film deposition uses alcohols as solvent in coating solutions in order to make homogeneous solutions of hydrophobic alkoxides and water. Alcohols, however, are volatile, inflammable, and hence not favorable solvents to be handled in industries. Therefore, replacement of alcohols by water as solvent is strongly demanded in industries. Unfortunately water has significantly high surface tension (72 mN m⁻¹) compared to alcohols (20-23 mN m⁻¹), causing poor wettability of the substrates and poor gel film formability. Recently, the authors demonstrated that the film formation ability is greatly enhanced when organic polymers with amide groups like polyvinylpyrrolidone (PVP, Fig. 1), polyvinylacetamide and polyacrylamide are added to aqueous solutions of metal salts [1]. Transparent TiO₂ and ZrO₂ ceramic coatings could be prepared from Ti(SO₄)₂ - H₂SO₄ - H₂O and ZrCl₂O - H₂O solutions containing these polymers [1], and were demonstrated to be as high in density and surface smoothness as those prepared by conventional alkoxide-based sol-gel method [2].

In the present study, the organic polymer-assisted aqueous solution-based sol-gel coating technique was applied to preparation of complex oxide thin films. In conventional alkoxide-based sol-gel method, single-phase complex oxides cannot be easily achieved due to the

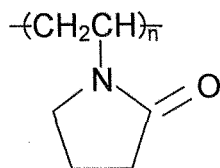


Fig. 1 PVP

difference in the rate of the hydrolysis and condensation reactions between alkoxides. Reaction rate control by chemical modification of alkoxides, or complex alkoxide synthesis should be performed beforehand. On the other hand, the organic polymer-assisted aqueous solution-based sol-gel technique provides a simple route where single-phase complex oxide thin films are easily obtained by dissolving the corresponding metal salts and organic polymers, which will be presented for the first time in the present paper, taking NiFe₂O₄, Y₃Fe₅O₁₂, LaCoO₃ and BaTiO₃ films as examples.

2. EXPERIMENTAL

For preparing NiFe₂O₄, Y₃Fe₅O₁₂ and LaCoO₃ films, Ni(CH₃COO)₂·4H₂O, Fe(NO₃)₃·9H₂O, Y(NO₃)₃·6H₂O, La(NO₃)₃·6H₂O, Co(NO₃)₂·6H₂O, PVP (K90, 10⁴ in viscosity average molecular weight) and ion-exchanged water were used as the starting materials. Fig. 2 shows the procedure for preparing the coating

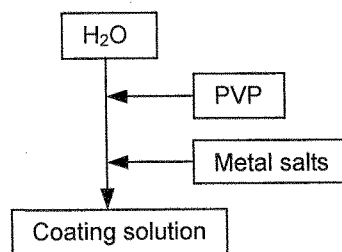


Fig. 2 Flow chart showing preparation of the coating solutions. In the case of the solution for BaTiO₃ films, PVP was added after the aqueous solution of metal salts was prepared.

solutions. Solutions of molar compositions, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O} : \text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} : \text{PVP} : \text{H}_2\text{O} = 1 : 2 : 1.5 : 150$, $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O} : \text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} : \text{PVP} : \text{H}_2\text{O} = 3 : 5 : 8 : 450$ and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O} : \text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} : \text{PVP} : \text{H}_2\text{O} = 1 : 1 : 1 : 300$ were prepared, where the mole ratio for PVP is defined for the monomer. Dip-coating was conducted on SiO_2 glass and single-crystal Si(100) substrates at a withdrawal rate of 0.5 cm min^{-1} . The gel films were immediately transferred into an electric furnace of 700 or 800°C, and fired there for 10 min. The gel film deposition and firing were cycled several times.

For preparing BaTiO_3 films, $\text{Ba}(\text{CH}_3\text{COO})_2$, 50wt% aqueous solution of titanium(IV) bis(ammonium lactato)dihydroxide $(\text{CH}_3\text{CH}(\text{O}-\text{NH}_4)_2\text{Ti}(\text{OH})_2$, PVP (K90, 6.3×10^5 in viscosity average molecular weight) and ion-exchanged water were used as the starting materials. A solution of molar composition, $\text{Ba}(\text{CH}_3\text{COO})_2 : (\text{CH}_3\text{CH}(\text{O}-\text{NH}_4)_2\text{Ti}(\text{OH})_2 : \text{PVP} : \text{H}_2\text{O} = 1 : 1 : 1 : 100.8$ were prepared, where PVP was added to the mixture of the aqueous solutions of $\text{Ba}(\text{CH}_3\text{COO})_2$ and $(\text{CH}_3\text{CH}(\text{O}-\text{NH}_4)_2\text{Ti}(\text{OH})_2$. Spin-coating was conducted on SiO_2 glass substrates at 1000 rpm. The gel films were heated up to 700°C at a rate of 5°C min^{-1} or fired at 700°C for 10 min.

3. RESULTS

An NiFe_2O_4 film was prepared on an SiO_2 glass substrate by repeating the dip-coating and firing (700°C, 10 min) ten times. The film obtained was dark brown

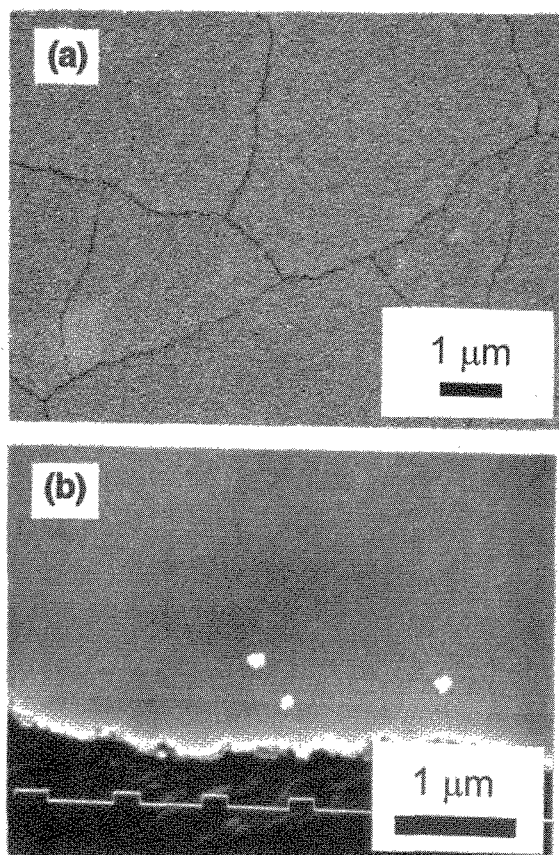


Fig. 3 SEM pictures of the NiFe_2O_4 films deposited on (a) SiO_2 glass and (b) single-crystal Si substrates. The films were prepared by repeating the dip-coating and firing (700°C, 10 min) ten times.

and transparent, 0.23 μm thick and single-phase NiFe_2O_4 . Macroscopic cracks were not detectable with the naked eyes or an optical microscope, while microcracks were observed in the SEM image (Fig. 3 (a)). When the film was deposited on a single-crystal Si substrate, on the other hand, no microcracks formed as seen in Fig. 3 (b), where the film was 0.3 μm thick and again NiFe_2O_4 in single-phase (Fig. 4 (a)).

A $\text{Y}_3\text{Fe}_5\text{O}_{12}$ film was deposited on an SiO_2 glass substrate by repeating the dip-coating and firing (1000°C, 10 min) ten times. The resultant film was yellowish brown, transparent, 0.22 μm thick and a mixture of cubic, tetragonal and orthorhombic $\text{Y}_3\text{Fe}_5\text{O}_{12}$. As in the case of the NiFe_2O_4 film, macroscopic cracks were absent, while microcracks were detected in the SEM image (Fig. 5 (a)). Deposition on single-crystal Si substrates was also conducted by repeating the gel film deposition and firing at 1000°C five times, where Fe_3O_4 was

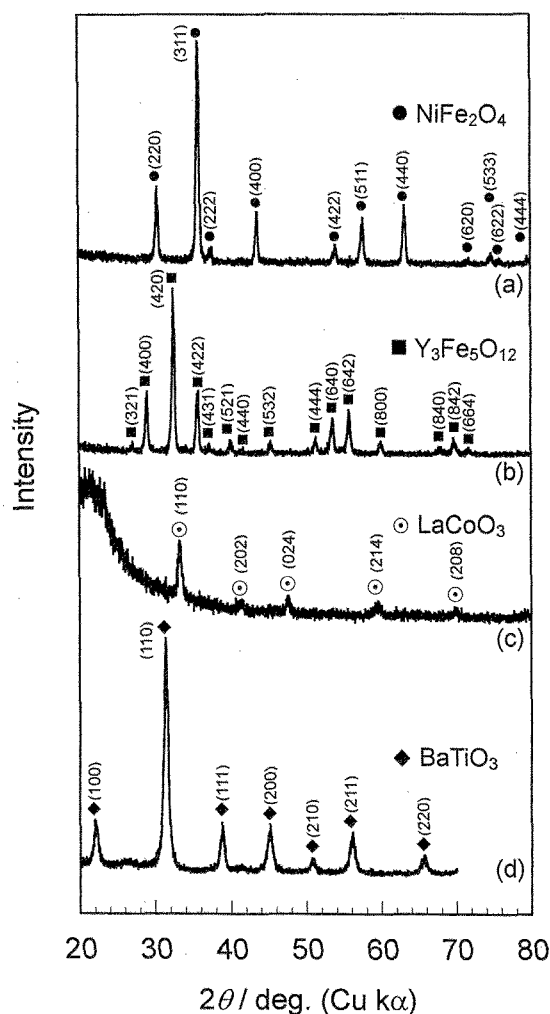


Fig. 4 XRD patterns of the fired films. (a) NiFe_2O_4 film prepared on an Si substrate via ten cycles of dip-coating and firing at 700°C, (b) $\text{Y}_3\text{Fe}_5\text{O}_{12}$ film on an Si substrate via five cycles of dip-coating and firing at 800°C, (c) LaCoO_3 film on an SiO_2 glass substrate via five cycles of dip-coating and firing at 700°C, and (d) BaTiO_3 film on an SiO_2 glass substrate by heating up to 700°C at a rate of 5°C min^{-1} .

precipitated as well as cubic $Y_3Fe_5O_{12}$. When firing was performed at 800°C in the deposition cycles, single-phase cubic $Y_3Fe_5O_{12}$ resulted on Si substrates (Fig. 4 (b)), where no microscopic cracks were observed (Fig. 5 (b)).

An $LaCoO_3$ film was prepared on an SiO_2 substrate by repeating the dip-coating and firing (700°C , 10 min) five times. The film obtained was light black, transparent, and $0.05\ \mu\text{m}$ thick. Microscopic as well as macroscopic cracks were absent as seen in the SEM picture (Fig. 6). The film was $LaCoO_3$ in single-phase

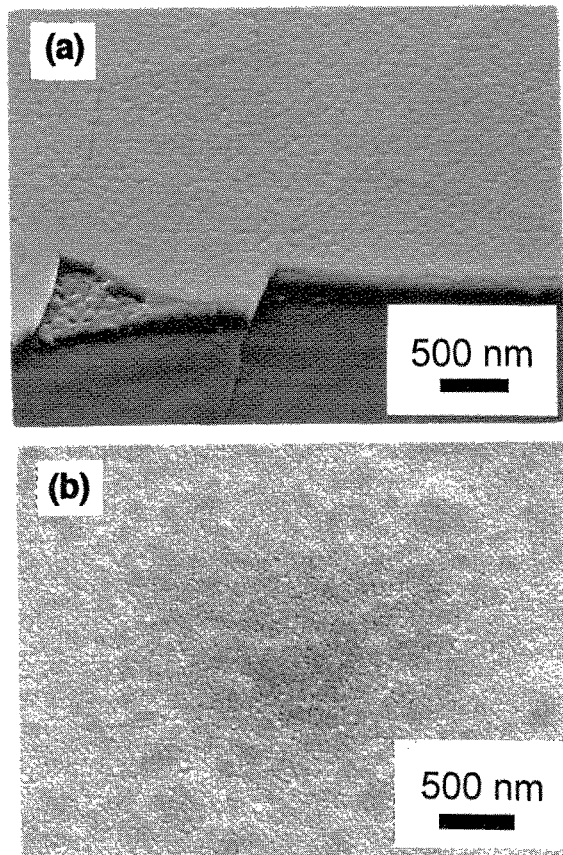


Fig. 5 SEM pictures of the $Y_3Fe_5O_{12}$ films. (a) On an SiO_2 glass substrate via ten deposition cycles with firing at 1000°C for 10 min, and (b) on a single-crystal Si substrate via five deposition cycles with firing at 800°C for 10 min

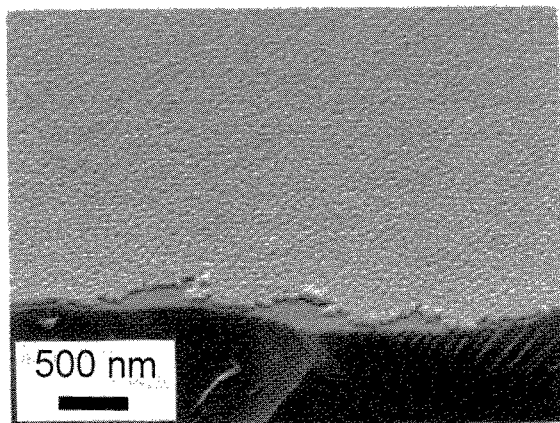


Fig. 6 SEM picture of the $LaCoO_3$ film deposited on an SiO_2 glass via five cycles of dip-coating and firing at 700°C for 10 min,

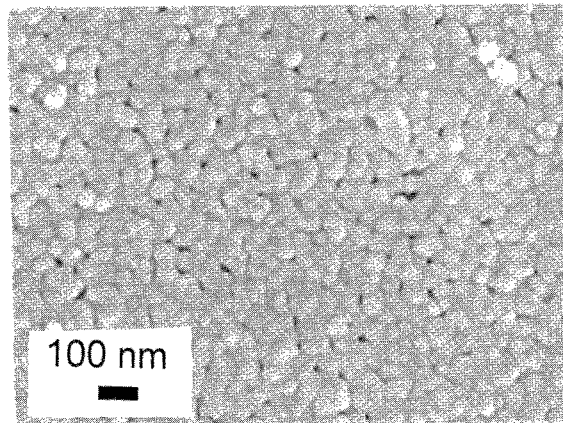


Fig. 7 SEM picture of the $BaTiO_3$ film deposited on an SiO_2 glass via non-cycled spin-coating and firing. The gel film was heated up to 700°C at a rate of 5°C min^{-1} .

as shown in Fig. 4 (c) where X-ray scattering from the glass substrate was detected centering at 22° due to the small thickness of the film.

A $BaTiO_3$ film was deposited on a SiO_2 substrate by spin-coating followed by firing at 700°C for 10 min. The gel film deposition and firing were not repeated, performed just once. The film was colorless, transparent, $0.5\ \mu\text{m}$ in thickness, and single-phase pseudocubic $BaTiO_3$ as seen in the XRD pattern (Fig. 4 (d)). When the gel film was heated up to 700°C at a rate of 5°C min^{-1} , where PVP was more slowly decomposed, a crack-free, $0.3\ \mu\text{m}$ thick film resulted as shown in Fig. 7.

4. DISCUSSION

The present experimental results demonstrated that PVP allows formation of single-phase complex oxide thin films from aqueous solutions of metal salts, where $NiFe_2O_4$, $Y_3Fe_5O_{12}$, $LaCoO_3$ and $BaTiO_3$ films were taken as examples. Sol-gel-derived oxide films of these compositions have been, of course, already reported in literature. Schleich and Zhang prepared $NiFe_2O_4$ films from ethylene glycol solution of nitrates [3], and Sedlar and Pust fabricated Co-doped $NiFe_2O_4$ films from ethylene glycol and 2-methoxyethanol solution of nitrates [4]. Kato et al. used ethylene glycol solution of nitrates containing ethyl acetoacetate for preparing Bi and Al-doped $Y_3Fe_5O_{12}$ films [5], and Matsumoto et al. from solutions containing nitrates, ethylene glycol and nitric acid [6]. For preparing $LaCoO_3$ films, Hwang et al. employed solutions of lanthanum alkoxide and cobalt nitrate containing 2-methoxyethanol and polyethylene glycol or ethyl acetoacetate [7,8], and Bontempi et al. used lanthanum nitrate and cobalt acetate dissolved in methanol [9]. Trummer et al. prepared $LaNi_xCo_{1-x}O_3$ films from solutions containing nitrates, ethanol and butylacetate [10]. As far as $BaTiO_3$ films are concerned, besides many papers on alkoxide-derived coatings, Lee and Zhang employed barium acetate dissolved in acetic acid where water-soluble titanium(IV) bis(ammonium lactato)dihydroxide was added, followed by dilution by water and ethanol [11].

As listed above, even when water-soluble metal salts are used as the material source, alcohols are always used as solvent, which may improve the

wettability of substrates. In that sense, the technique presented here is a unique one, which uses only water as the solvent. However, there is one exceptional example in literature; Zhang et al. prepared LaCoO_3 thin films from aqueous solution of $\text{LaCo}(\text{DPTA})\cdot 6\text{H}_2\text{O}$ containing polyethylene glycol, where DPTA is dithylenetriaminepentaacetic acid [12].

The C=O groups of PVP can coordinate the metal atoms, and also can make hydrogen bonds with H_2O molecules and/or OH ions that coordinate the metal atoms, forming loosely bonded organic-inorganic hybrid polymers. The C=O groups of PVP can also make hydrogen bonds with the OH groups of the substrate surface, which might improve the wettability, and allow the formation of homogeneous gel films as was discussed in a previous paper [2]. The more important point to be addressed here is the formation of single-phase complex oxides aided by PVP. As was mentioned above, the C=O groups of PVP could coordinate the metal atoms and also could make hydrogen bonds with H_2O and/or OH ligands of the metal complexes. This might achieve high homogeneity in metal atom distribution in solutions and in gel films, facilitating the formation of single-phase complex oxides. It is thought that polyethylene glycol employed by Zhang et al. [12] may have similar function in formation of complex oxide films to PVP, where ether groups might make hydrogen bonds and/or act as ligands.

When deposited on SiO_2 glass substrates, NiFe_2O_4 and $\text{Y}_3\text{Fe}_5\text{O}_{12}$ films had microcracks in SEM images. The substrate, SiO_2 glass, has much smaller thermal expansion coefficient ($0.55 \times 10^{-6} \text{ K}^{-1}$ [13]) than NiFe_2O_4 ($(9-13) \times 10^{-6} \text{ K}^{-1}$ [14]) and $\text{Y}_3\text{Fe}_5\text{O}_{12}$ ($(9-11) \times 10^{-6} \text{ K}^{-1}$ [15]). Also, the microcracks are zigzag in shape, propagating along the grain boundaries (Fig. 3 (a) and 5 (a)), indicating the occurrence of cracking at least after crystallization. Therefore, the in-plane thermal stress in films, which is tensile, generated on cooling is thought to have caused the microcracking. When these films were deposited on Si substrates, on the other hand, microcracking did not occur, which may be due to the larger thermal expansion coefficient of Si ($2.5 \times 10^{-6} \text{ K}^{-1}$ [16]) than SiO_2 glass. Although LaCoO_3 and BaTiO_3 have much larger thermal expansion coefficient ($23 \times 10^{-6} \text{ K}^{-1}$ [17] and $14 \times 10^{-6} \text{ K}^{-1}$ [13], respectively) than SiO_2 glass, they had no microcracks even when deposited on SiO_2 glass substrates. The exact reasons for the absence of microcracks are not yet clear, but the extremely small thickness, and possible porous nature could be the causes for the LaCoO_3 film and the BaTiO_3 film, respectively.

5. CONCLUSIONS

PVP-assisted aqueous solution-based sol-gel technique has been demonstrated to be available for preparing complex oxide coating films.

- (1) Crack-free, 0.3 μm thick NiFe_2O_4 films could be prepared on Si substrates from an $\text{Ni}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ - $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ - PVP - H_2O solution via ten time deposition cycles.
- (2) Crack-free $\text{Y}_3\text{Fe}_5\text{O}_{12}$ were obtained on Si substrates from a $\text{Y}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ - $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ - PVP - H_2O solution via five time deposition cycles.
- (3) Crack-free, 0.05 μm thick LaCoO_3 films could be obtained on SiO_2 glass substrates from an $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ - $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ - PVP - H_2O

solution via five time deposition cycles.

- (4) Crack-free, 0.3 μm thick pseudocubic BaTiO_3 films could be prepared on SiO_2 glass substrates from a $\text{Ba}(\text{CH}_3\text{COO})_2$ - $(\text{CH}_3\text{CH}(\text{O})\text{NH}_4)_2\text{Ti}(\text{OH})_2$ - PVP - H_2O solution via non-repetitive deposition.
- (5) NiFe_2O_4 and $\text{Y}_3\text{Fe}_5\text{O}_{12}$ films had microscopic cracks when deposited on SiO_2 glass substrates, which may be due to thermal stress generated on cooling. These microcracking could be avoided when the films were deposited on Si substrates having a larger thermal expansion coefficient than SiO_2 glass.

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