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Dip coating of PT, PZ and PZT films using an alkoxide–diethanolamine method

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Dip-coating of uniform PT, PZ and PZT films was investigated using a solution of titanium tetraisopropoxide (and/or zirconium *n*-butoxide), diethanolamine, lead acetate trihydrate and isopropanol, where the diethanolamine/alkoxide molar ratio $R = 1$ and the water/alkoxide molar ratio $W = 3$. Perovskite-type PT and PZT films were obtained on glass substrates above 500 to 600° C when the solutions with concentrations equal to or higher than 0.4 M were used as the dip solution. The resistivity of the films formed was larger than $10^8\,\Omega$ cm when they were fired around 600° C. The dielectric constants (dielectric loss tangents) were found to be 264 (0.03) for PT, 214 (0.05) for PZT and 158 (0.02) for PZ.

1. Introduction

In our previous papers [1–3], we reported that glycols or alkanolamines were very effective to prepare uniform and dense oxide films from an alcoholic solution of alkoxides, suggesting that this system could be extended to the preparation of multi-component oxide films, because alkanolamine–alkoxide systems were very stable to hydrolysis, and the alkanolamines had the dissolving power of many inorganic salts. In fact, lead acetate can be dissolved in a solution of alkoxide–diethanolamine–alcohol to give a clear solution which was found to be very stable and be suitable for the dip-coating of PT, PZ and PZT films.

So far, only a few reports [4, 5] on the dip-coating of these films have been published. Our dip-solution can be easily prepared and is very stable. In this paper we report the details of our study on the dip-coating of PT, PZT and PZ films using these solutions.

2. Experimental procedure

Commercial titanium tetraisopropoxide (TIP), zirconium tetra(*n*-butoxide) (ZNB), diethanolamine (DEA), isopropanol (water content < 0.1%), and lead acetate trihydrate, were used without further purification.

An equimolar concentration of DEA was added to the isopropanol solution of the alkoxide TIP or ZNB (0.1 to 0.7 M) under a nitrogen atmosphere and the solution was stirred for 1 h at room temperature. Then lead acetate trihydrate powder was added to the solution with stirring. It dissolved in the solution within 1 h at room temperature to give a clear solution. In the absence of DEA it is insoluble in the alcohol. The resultant clear solutions were used as the PT or PZ dip-solutions. In the preparation of PZT solutions, appropriate amounts of PT solution were mixed with PZ solution.

The substrate plates used in this study were glass (Corning Co. no. 7059), alumina single crystal and platinum plates. These plates were cleaned before use by washing with acetone. Typical dimensions of the substrate plate were $10 \times 40\,\mathrm{mm}^2$ for the glass and platinum, and $10 \sim 20\phi$ for the alumina single crystal. The plate was dipped into the solution, drawn up at constant speed (typically $18\,\mathrm{cm\,min}^{-1}$) and dried in air at 100° C for 10 to 30 min. The dried gel films were fired at 400 to 1000° C for 1 h in air. Thick films were prepared by repeating the above coating cycle, but a draw-up speed of $6\,\mathrm{cm\,min}^{-1}$ was used, because the stacking of thick films sometimes caused cracks in the films formed.

The resultant films were examined by X-ray diffraction (XRD), electron spectroscopy for chemical analysis (ESCA), SEM and TEM. For infrared (IR) examination, films on KBr single crystals were used. The electrical properties across the films on platinum plates were examined using a conventional impedance bridge. The contacts were applied by evaporating gold on to limited areas ($5 \times 5\,\mathrm{mm}^2$) of the films and painting silver paste on the gold film to attach copper wire leads.

3. Results and discussion

As previously reported [1, 3, 6, 7], alcoholic solutions of TIP and ZNB are very unstable to hydrolysis. So, upon addition of water, particularly on the addition of an excess amount of water, white oxides or basic oxides precipitate quickly. However, when an equimolar amount of DEA to the alkoxide was added, the solution could be stabilized, so that a homogeneous solution was obtained even on the addition of water. To prepare uniform oxide films, the addition of water seems to be indispensable, otherwise the resultant films have many cracks. Water assists in the formation

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of metal-oxide polymer by partial hydrolysis and subsequent polymerization of hydrolysed species [8–10]. The effect of DEA is to keep the hydrolysed species in the solution. DEA has another important effect, in dissolving lead acetate trihydrate into the alcohol. In the presence of DEA, therefore, an alkoxide–lead acetate–alcohol solution can be obtained. Without further addition of excess water, the water/alkoxide molar ratio (W) in the solution can be fixed at 3, and the water content is sufficient to prepare uniform films. The solution can be stored for as long as half a year without appreciable change in the transparency and the viscosity of the solution.

When excess water was added to the PZT solution, the solution gelled. The water content required to induce gelation varied depending on the PT content in the solution, as shown in Fig. 1. At $W = 10$, pure PT solution gelled quickly, but pure PZ solution remained unchanged even after 1000 h. The mixture of 50 mol % PT and PZ gelled after about 6 h.

Using the dry gel which was composed of 50 mol % PT and 50 mol % PZ, i.e. PZT gel, we studied the variation of X-ray diffraction patterns of the gel with heating temperature between 100 and 1000° C in air as shown in Fig. 2. The heating time at each temperature was 1 h. At 300° C, very sharp peaks assignable to metallic lead were observed. PZT gel was converted to lead oxide (PbO) at 400° C and to perovskite PZT at higher temperatures. A temperature of 600° C seems to be required to obtain the PZT from the gel. Other PT and PZ gels behaved similarly. Therefore, the lowest heating temperature was fixed at 500 to 600° C to prepare PT, PZ and PZT films.

Refluxing the original solution had no effect on the decomposition properties of the dry gel. All powders derived from the gels were crystallized as perovskite but not as pyrochlore. Blum and Gurkovich [11] found an unknown phase in the PT powder around 400° C. This phase might be metallic lead or lead oxide although its identification is still in doubt.

The weight change of the PZT gel during heat-treatment in air is shown in Fig. 3. At 300° C a black lump was formed, which disintegrated into a fine powder and was discoloured to orange at 400° C, yellow at 500° C, pale yellow at 600° C and finally white at 700° C. The final weight at 700° C was 60%, suggesting that the gel contained organic groups corresponding to a total molecular weight of about 217 per PZT unit. This corresponds to one mole of DEA (mol.wt 105) and some fractions of the acetate group (mol.wt 59) and/or isopropyl group (mol.wt 59) and water. The small weight increase observed between 400 and 500° C is attributable to the oxidation of metallic lead into the oxide as described above. IR analysis of the dry gel films formed on KBr single crystals showed the presence of acetate groups and other organic moieties which disappeared when heated above 300° C.

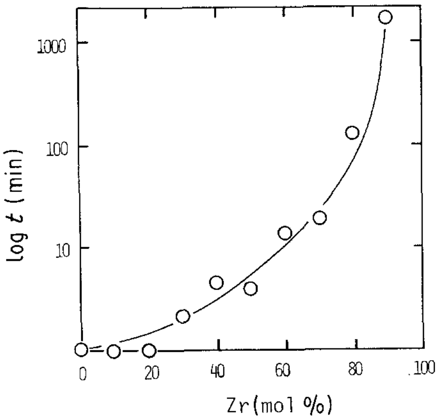

Figure 1 Gelation time plotted against the composition of PZ_xT_{1-x} solutions of 0.5 M alkoxide, $R = 1$ and $W = 10$ at room temperature.

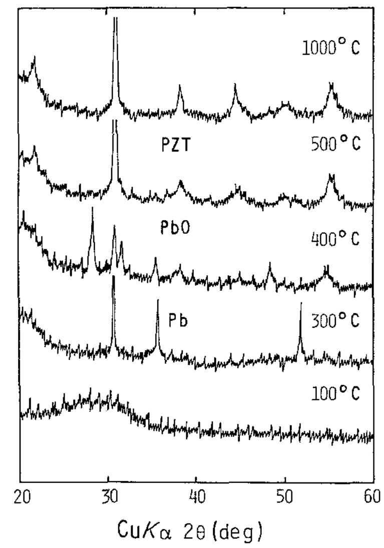

Figure 2 Temperature dependence of XRD pattern of PZT gels obtained at room temperature from the solution of 0.5 M TTIP, ZNB and $Pb(OAc)_2 \cdot 3H_2O$ at $R = 1$ and $W = 20$.

The XRD patterns of multi-coated films at various temperatures were very similar to those of PZT gels, and perovskite PZT film formation was confirmed at 600° C, when the PZT concentration of the solution was equal to or higher than 0.4 M. The diffraction peaks due to metallic lead were not observed, different from the case of the gel, probably because of its rapid oxidation in thin films. Here it is very interesting to note that XRD patterns of the films strongly depended on the concentration of the dip solutions and the substrates used. The concentration dependence of the XRD patterns of the films on glass at 600° C is shown in Fig. 4. For the films obtained at lower concentrations, broad diffraction peaks are observed, which cannot be assigned to perovskite PZT. The diffraction pattern of the film derived from 0.1 M solution is consistent with that of cubic crystal, pyrochlore. The intensity of the peaks assignable to the pyrochlore decreased with increasing PZT concentration of the solution, and at about 0.4 M only perovskite PZT was formed. On the other hand, complete perovskite PZT formation was found on the platinum plate even at lower PZT concentrations, for example 0.2 M, as shown in Fig. 5. The films coated on alumina single crystals under the same conditions were identified as perovskite PZT, similar to those on platinum plates. The solutions with PZT concentrations equal to or higher than about 0.4 M tended to afford perovskite PZT films on common substrates.

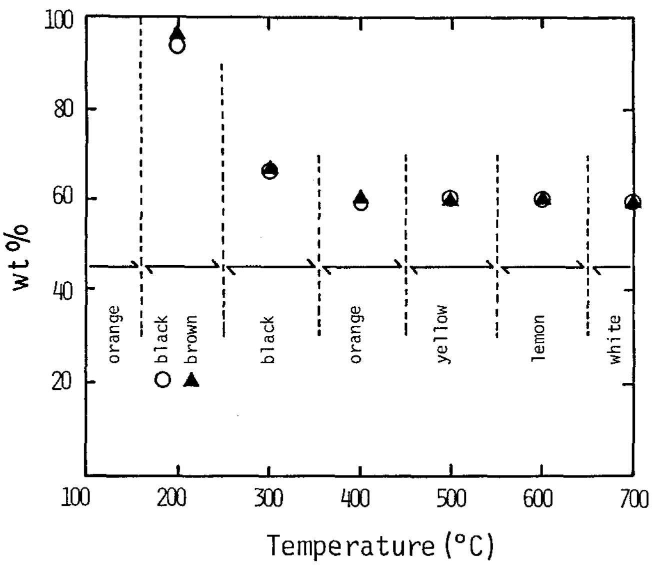

Figure 3 Variation of the weight percentage and the appearance of PZT gels with heating temperature. PZT was heated in air at each temperature for 2 h. (○) Gel obtained after reaction at room temperature, (▲) gel obtained after refluxing the solution.

In the case of PT films on glass, very similar trends also existed. 0.1 M solution gave pure pyrochlore at 500° C irrespective of coating cycle times, but more concentrated solutions perovskite PT, as in the case of PZT. Even on platinum plates the 0.1 M PT solution yielded pyrochlore film. So far, no pyrochlore formation has been found in the sol–gel process, only in the sputtering process [12–14]. This pyrochlore is considered to be a metastable phase in nature. In fact, the pyrochlore thin films on glass could be converted to perovskite PT when heated in air at 700° C for 25 h.

ESCA analysis (depth profile) of PZT films on glass showed that lead ions in the films diffused deeply into the substrate. It can be assumed that the resultant depletion of lead ions in the films caused the formation of the pyrochlore films. However, examination of XRDs of the powders which were derived from the solution with various Pb/(Ti + Zr) ratios (0.7 to 1.3) gave no conclusive evidence of the formation of a particular phase, other than the perovskite. Therefore, the formation of pyrochlore, especially on a glass substrate may be attributable to the effect of thin films, in other words, the surface energy effect. In the case of an amorphous substrate, this effect would act strongly. Crystalline structures such as platinum and alumina, on the other hand, can accelerate the crystallization into the perovskite by their epitaxial effect. In the case of very thin PT films, the effect of the film might be superior to the substrate effect, because 0.1 M solution yields pyrochlore even on a platinum plate. The lack of observation by other workers of the pyrochlore formation in the sol–gel process may be attributable to the fact that they used concentrated solutions or metallic substrates such as platinum and stainless steel. Although some ions could diffuse from the glass plate into the films and assist the formation of the metastable phase, we could not find the ions in the ESCA spectra of the films. Modification of the PT and PZT films will be discussed in a subsequent paper [15].

The composition dependence of the crystal form of $Pb(Zr_xTi_{1-x})O_3$ powders formed from the gels is shown in Fig. 6. At about $x = 0.5$ the crystal form varied from tetragonal to rhombohedral, consistent with the results obtained in powder reaction [16]. The lattice constants of PT at room temperature are in good agreement with those in the literature, as shown in Fig. 6. High-temperature XRD patterns of PT

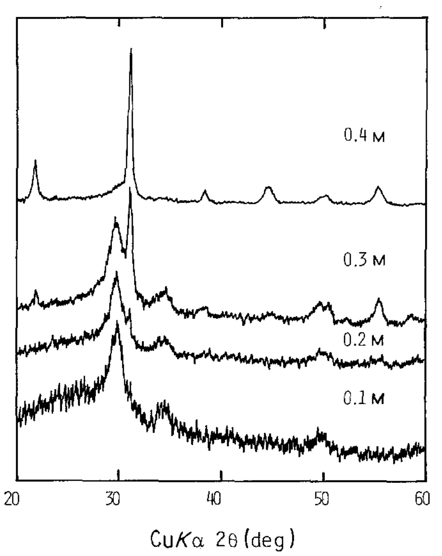

Figure 4 Effect of PZT concentration (R = 1 and W = 3) on XRD pattern of PZT films formed on glass plates at 600° C. Broad peaks can be assigned to the pyrochlore.

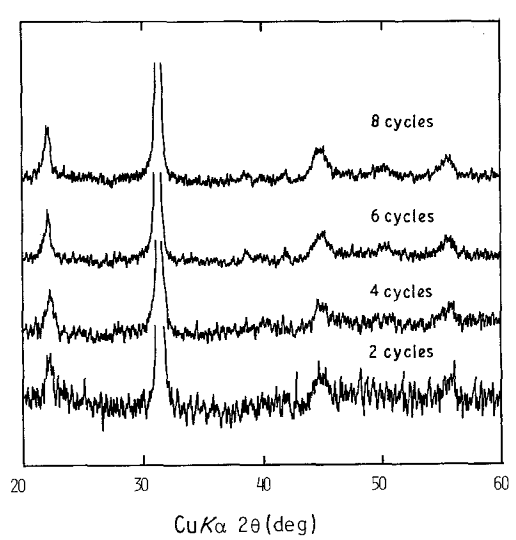

Figure 5 XRD patterns of PZT films formed on platinum plates by various coating cycles at 600° C using 0.2 M solution (R = 1, W = 3).

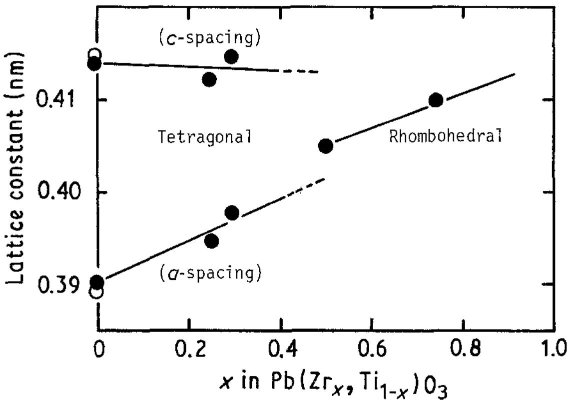

Figure 6 Composition dependence of the crystal form and lattice constants of $Pb(Zr_xTi_{1-x})O_3$ powders formed from the gels ($R = 1$ and $W = 3$). (○) ASTM data for PT.

powders formed from the gels are shown in Fig. 7, suggesting that the cubic phase was formed around 450° C, consistent with the literature [17]. Very similar trends were observed in the case of films. These observations strongly confirm that these sol–gel processes can yield very homogeneous PT and PZT films. The composition of PZT powders (ICP emission analysis: PbO 68.8%, TiO_2 12.5% and ZrO_2 18.6%) obtained by heating a PZT gel at 1000° C for 1 h was very close to that of PZT (PbO 68.5%, TiO_2 12.3% and ZrO_2 19.2%), suggesting no loss of lead species during the heat treatment.

The variation in thickness of the films obtained on glass substrates by one coating cycle with the PZT concentration is shown in Fig. 8. The film thickness was linearly proportional to the PZT concentration. At 0.5 M, uniform and transparent films about 200 nm thick were obtained. The films obtained from more concentrated solutions tended to have fine cracks. Therefore, the maximum thickness of uniform films obtainable by one coating cycle seems to be about 180 to 200 nm. The film thickness evaluated from the film weight on unit substrate area and the theoretical density of perovskite PZT ($7.99\,g\,cm^{-3}$) was in good agreement with that from SEM observations, suggesting that the films were well densified. As described above, the films derived from the solution with a concentration between 0.1 and 0.3 M should contain large fractions of pyrochlore. Therefore, when perovskite PZT film on glass are required, 0.4 to 0.5 M solutions should be used. In all cases, higher temperatures are more inducive to the formation of the perovskite form, similar to the sputtering.

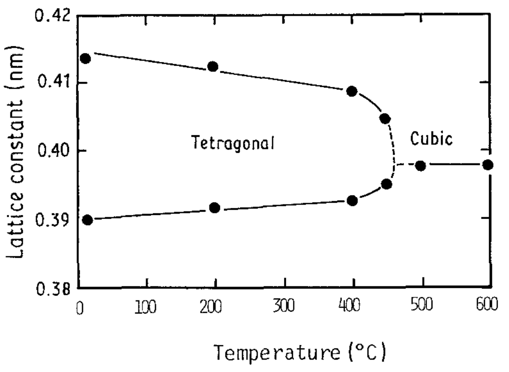

Figure 7 Lattice constants of a PT disc as a function of temperature.

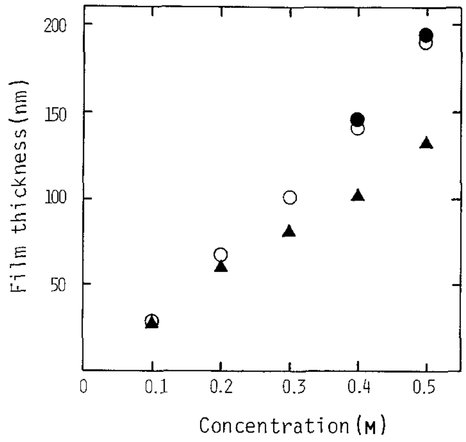

Figure 8 Thickness variation of PZT films formed on glass plates at 600° C with the concentration of PZT solution ($R = 1$ and $W = 3$). The thickness was evaluated by three different methods: (○) from the theoretical density of PZT; (●) from the SEM image of the cross section, and (▲) from surface roughness meter (Talysurf). The values obtained by Talysurf were smaller than those obtained by other methods due to the softness of PZT films.

Electrical properties of PT, PZ and PZT films (film thickness ~1.5 μm) formed at 600° C were measured across the film thickness using an impedance bridge. The typical electrical resistivities and dielectric constants evaluated for a parallel-equivalent circuit are shown in Table I. All films have electrical resistivities larger than $10^8\,\Omega\,cm$. The dielectric constants had a tendency to decrease with increasing zirconium content.

This sol–gel process can be extended to the preparation of other useful films such as PLZT and niobium-doped PZT, because lanthanum nitrate is soluble in the solution, and because other metal alkoxides can be added without difficulty. The solution has the advantages that it can be easily prepared at room temperature and it is stable enough to be handled in air.

4. Conclusions

Thin film preparation of PT, PZ and PZT was investigated by dip-coating using a solution composed of titanium tetraisopropoxide (zirconium *n*-butoxide), diethanolamine, lead acetate trihydrate and isopropanol. The following results were obtained.

1. The solution with a diethanolamine/alkoxide molar ratio of 1 and water/alkoxide molar ratio of 3 was so stable that the solution could be stored for as long as half a year without appreciable change in viscosity.

2. The crystal structure of PT and PZT films strongly depend on the concentration of the solution and the substrate used. 0.2 M solution gave only pyrochlore on

TABLE I The electrical properties of the films prepared on platinum plates at 600° C (measured using an impedance bridge at 1 kHz)

Film	Dielectric constant	tan δ	Resistivity ($10^8\,\Omega\,cm$)
PT	264	0.03	2.4
PZT	214	0.15	1.7
PZ	158	0.02	6.4

glass at about 600° C, but gave perovskite on a platinum plate. The perovskite content in the film on glass increased with increasing concentration of the solution, and hence above 0.4 M only perovskite was formed on glass.

3. 0.1 M PT solution yielded pyrochlore on both glass and platinum plates.

4. The maximum thickness of uniform perovskite PZT films obtained on glass by one coating cycle was limited to about 180 to 200 nm.

5. The perovskite PZT films on platinum showed a resistivity larger than $10^8\ \Omega$ cm when they were fired at about 600° C. Dielectric constants (dielectric loss tangents) were 264 (0.03) for PT, 214 (0.05) for PZT and 158 (0.02) for PZ.

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