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PVP-assisted sol-gel deposition of single layer ferroelectric thin films over submicron or micron in thickness

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Abstract

PZT, $BaTiO_3$ and $BaBi_4Ti_4O_{15}$ films were prepared on Pt/Ti/SiO_2/Si substrates by spin-coating using alkoxide solutions containing polyvinylpyrrolidone (PVP). Deposition and firing of the gel films were performed just once, not repeated. Crack-free, single-phase PZT, $BaTiO_3$ and $BaBi_4Ti_4O_{15}$ films as thick as 2.2, 0.77 and 0.40 μm could be prepared, respectively, via non-repetitive spin-coating. The 2.2 μm thick PZT film exhibited *P–E* hysteresis with remanent polarization and coersive field of 21 $\mu C\ cm^{-2}$ and 90 $kV\ cm^{-1}$, respectively. The dielectric constant of the PZT, $BaTiO_3$ and $BaBi_4Ti_4O_{15}$ films were 370, 310 and 380, respectively, at 1 kHz.

Keywords: $BaTiO_3$ and titanates; Dielectric properties; Films; PZT; Sol-gel processes

1. Introduction

Ceramic coating films of ferroelectric functions often require submicron thickness or over.[1] However, conventional sol-gel coating normally allows crack-free films only less than 0.1 μm in thickness; thicker films undergo cracking and/or delamination on gel-to-ceramic film conversion. In order to avoid cracking or delamination, cycles of gel film deposition and firing are employed in laboratories using sols of low viscosities, limiting the single layer thickness below 0.1 μm. Such repetitive deposition, however, is time-consuming and impracticable in industries.

Although the low uncracking critical thickness is the critical issue for sol-gel production of ceramic coatings, the origins of the cracking have not been extensively studied. Recently the authors have made in situ observation on alkoxide-derived silica and titania gel films deposited on Si substrates, where the films were heated at constant rates in a near infrared furnace equipped with an optical microscope.[2] The films were found to be cracked in the heating-up stage at temperatures of 100–400 °C, depending on the film thickness and heating rate. This observation strongly suggested that the tensile stress resulting from film densification causes cracking although the origin of cracking is often attributed to the difference in thermal expansion coefficients between the film and the substrate.

Densification of gel films occurs via solvent evaporation and condensation reaction.[3] The authors expected that the strong hydrogen bonds between the amide groups of polyvinylpyrrolidone (PVP, Fig. 1) and the hydroxyl groups of the metalloxane polymers could hinder the condensation reaction in films, promoting the stress relaxation in the heating-up stage.[4] In fact, crack-free, over submicron thick films including PZT and $BaTiO_3$ could be fabricated from solutions containing PVP via non-cycled deposition.[2,4–12]

The present paper describes the most recent achievements in single-layer $BaTiO_3$ and PZT films prepared by the PVP-assisted sol-gel method. $BaBi_4Ti_4O_{15}$ films were also prepared, which is now attracting much attention as a lead-free ferroelectric material.

2. Experimental

2.1. Preparation of the coating films

PVP of 6.3×10^5 in viscosity average molecular weight (K-90) was used. PZT films were prepared from a solution of molar composition, $Pb(NO_3)_2$:$Zr(OC_3H_7^n)_4$:$Ti(OC_3H_7^i)_4$:PVP:$CH_3COCH_2COCH_3$:$CH_3OC_2H_4OH$:n-$C_3H_7OH = 1.1:0.53:0.47:1:0.5:30:0.98$. The mole ratio for PVP was defined for the monomer. First, $Pb(NO_3)_2$

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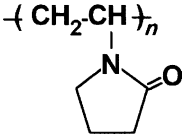

Fig. 1. PVP.

was dissolved in $CH_3OC_2H_4OH$, and then PVP, $Zr(OC_3H_7^n)_4$–n-C_3H_7OH solution and $Ti(OC_3H_7^i)_4$ were added to the solution in this sequence. In a previous work,[12] the solution thus prepared served as the coating solution with the addition of $CH_3COCH_2COCH_3$. In the present work the solution was concentrated in order to make the sol more viscous using a rotary pump until the weight loss reached 45%. Then the prescribed amount of $CH_3COCH_2COCH_3$ was added to the solution, and kept being stirred at room temperature in a sealed container for 20 h. The resultant solution 373 mPa s in viscosity was served as the coating solution.

$BaTiO_3$ films were prepared from a solution of molar composition, $Ba(CH_3COO)_2$:$Ti(OC_2H_5)_4$:PVP:CH_3COOH:H_2O:C_2H_5OH = 1:1:0.5:27:10:5. The as-prepared solution was kept standing in a sealed container for 100 h, and served as the coating solution.

$BaBi_4Ti_4O_{15}$ films were prepared from a solution of molar composition, $Ba(CH_3COO)_2$:$Bi(CH_3(CH_2)_3CH(C_2H_5)COO)_3$:$Ti(OC_3H_7^i)_4$:PVP:$CH_3(CH_2)_3CH(C_2H_5)COOH$:$H_2O$:$CH_3OC_2H_4OH$:$CH_3COOH$ = 1:4:4:4:5.48:4:75:27. First, PVP was dissolved in $CH_3OC_2H_4OH$, and then $Bi(CH_3(CH_2)_3CH(C_2H_5)COO)_3$–$CH_3(CH_2)_3CH(C_2H_5)COOH$ solution, $Ti(OC_3H_7^i)_4$, $Ba(CH_3COO)_2$–CH_3COOH solution, and H_2O were added in this sequence.

Gel films were deposited on Pt/Ti/SiO_2/Si substrates by spin-coating, and heat-treated in an electric furnace.

2.2. *Measurements and observations*

The thickness of the films was measured by a contact probe surface profilometer as described elsewhere.[4] Dielectric constants of the films were measured using an LCR meter. Polarization–electric field (*P*–*E*) characteristics were examined using a Sawyer–Tower bridge equipped with an oscilloscope. For these measurements, upper Pt electrodes of 0.2 mm in diameter were deposited on the surface of the films by sputtering.

3. Results and discussion

3.1. *PZT films*

In a previous work[12] crack-free PZT films as thick as 0.75 μm could be prepared from a $Pb(NO_3)_2$–$Zr(OC_3H_7^n)_4$ – $Ti(OC_3H_7^i)_4$ – H_2O – $CH_3COCH_2COCH_3$–$CH_3OC_2H_4OH$–n-C_3H_7OH solution containing PVP. The coating solution was stable in viscosity at around 50 mPa s for over 1300 h at room temperature, which was a benefit for industrial use. However, thicker films could not be made because of the low solution viscosity, and the viscosity could not be raised by reducing the solvent content because of the low solubility of $Pb(NO_3)_2$. It was found in the present work that the solvent could be evacuated after preparing $Pb(NO_3)_2$–$Zr(OC_3H_7^n)_4$–$Ti(OC_3H_7^i)_4$–PVP–$CH_3OC_2H_4OH$–n-C_3H_7OH solution. The solution remained transparent during evacuation. One possible reason for the concentration without precipitation is the formation of more soluble lead complexes in the presence of zirconium and titanium alkoxides.

A crack-free, transparent, 2.2 μm thick PZT film could be prepared by spin-coating from the concentrated solution 373 mPa s in viscosity via non-repetitive deposition. The substrate was spun at 500 rpm for 10 s and then at 1250 rpm for 60 s, and the gel film was heated in air successively at 80 °C for 10 min, 300 °C for 10 min and then at 700 °C for 10 min. The film was relatively dense, consisting of particles 40–50 nm in size (Fig. 2), and was crystallized in single-phase pseudo-cubic PZT as revelaed in the XRD pattern (Fig. 3), exhibiting *P*–*E* hysteresis with remanent polarization P_r of 21 μC cm^{-2} and coercive field E_c of 90 kV cm^{-1} at 60 Hz and 70 V (Fig. 4). The dielectric constant and loss tangent were 370 and 0.007, respectively, at 1 kHz. P_r and E_c were not large and small enough compared with those reported in the literature. For example, Sriprang et al. reported a larger P_r of 34 μC cm^{-1} and a smaller E_c of 54 kV cm^{-1} for a single-layer, 0.4 μm thick PZT film prepared by a triol-based sol-gel roulte.[13] Probably further densification should be achieved for the present films.

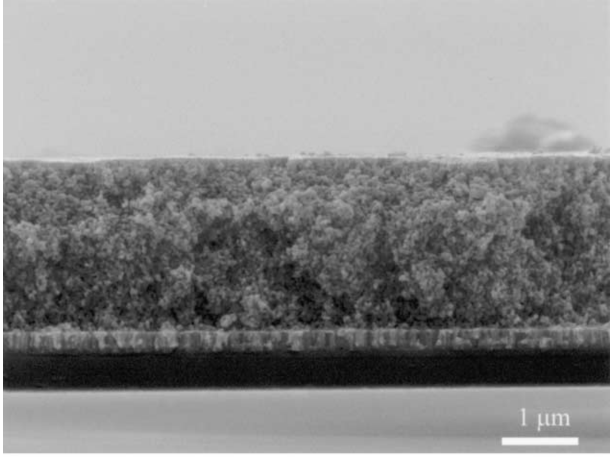

Fig. 2. SEM picture of the cross-section of the PZT film deposited on a Pt/Ti/SiO_2/Si substrate via non-repetitive, single step deposition.

3.2. $BaTiO_3$ films

In the works initially performed,[4,5] crack-free, single-layer $BaTiO_3$ films over 1 μm were achieved using a solution of molar ratio, $Ba(CH_3COO)_2$:$Ti(OC_3H_7^i)_4$:PVP:H_2O:CH_3COOH:i-C_3H_7OH = 1:1:1:20:9.08:20. However, the solution gelled within a few hours, not available in industrial use. Then in the next work[11] the composition of the solution was tailored, where stability in viscosity over 900 h could be achieved by replacing $Ti(OC_3H_7^i)_4$ and i-C_3H_7OH by $Ti(OC_2H_5)_4$ and C_2H_5OH, respectively, and increasing the amount of CH_3COOH. A single-phase $BaTiO_3$ films 0.56 μm in thickness could be prepared on nesa silica glass substrates via final heat-treatment at 700 °C, showing a dielectric constant of 290.[11]

In the present study, deposition on Pt/Ti/SiO_2/Si substrates and thicker film formation by spin-coating at low spinning rates were attempted using the same coating solution. Also the firing temperature was raised from 700 to 900 °C. The gel film was deposited on a Pt/Ti/SiO_2/Si substrate at a spinning rate of 500 rpm, and then was heated successively at 360 °C for 10 min and at 900 °C for 10 min. A 0.77 μm thick film could be obtained, consisting of particles 50–100 nm in size (Fig. 5). The film was almost single-phase pseudocubic $BaTiO_3$ (Fig. 3), and the dielectric constant and loss tangent were 310 and 0.05, respectively, at 1 kHz. The dielectric constants reported in the literature on gel-derived $BaTiO_3$ thin films are rather scattered, ranging from 100 to 500, and the present value of 310 can be said to be comparable with these values. However, Hayashi et al.[14] reported a dielectric constant of 1000 for gel-derived $BaTiO_3$ films, which is much larger than the present one. Probably further densification or increase in crystallinity would be needed for the present $BaTiO_3$ films.

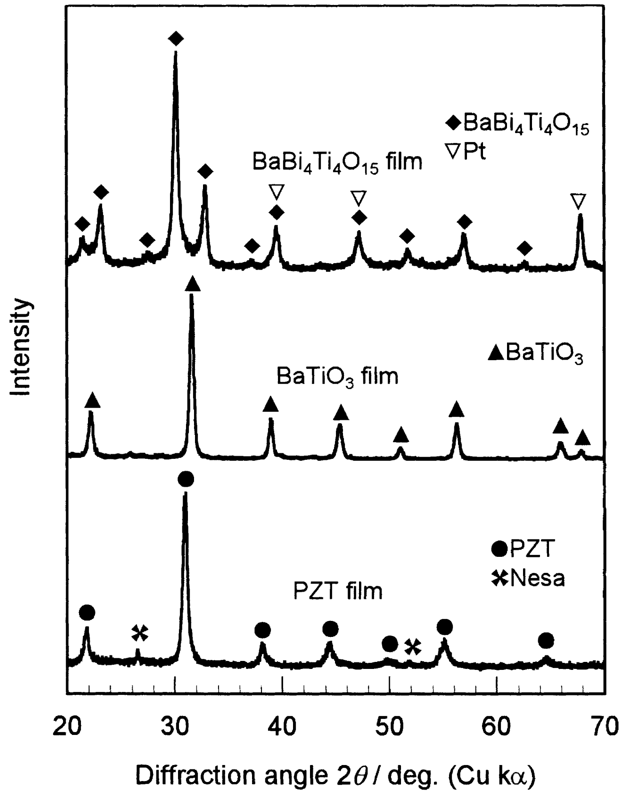

Fig. 3. XRD patterns of the PZT, $BaTiO_3$ and $BaBi_4Ti_4O_{15}$ films prepared via non-repetitive, single step deposition. The PZT film was deposited on nesa silica glass substrate.

3.3. $BaBi_4Ti_4O_{15}$ films

The precursor solution was found to be stable in viscosity at least over 300 h. Gel films were deposited on Pt/Ti/SiO_2/Si substrates by spin-coating at a spinning rate of 1000 rpm, and then heated successively at 300 °C for 10 min and at 800 °C for 10 min. A crack-free film 0.40 μm in thickness could be obtained. The film was somehow porous as revealed in the SEM picture (Fig. 6), crystallized in single-phase $BaBi_4Ti_4O_{15}$ (Fig. 3), and

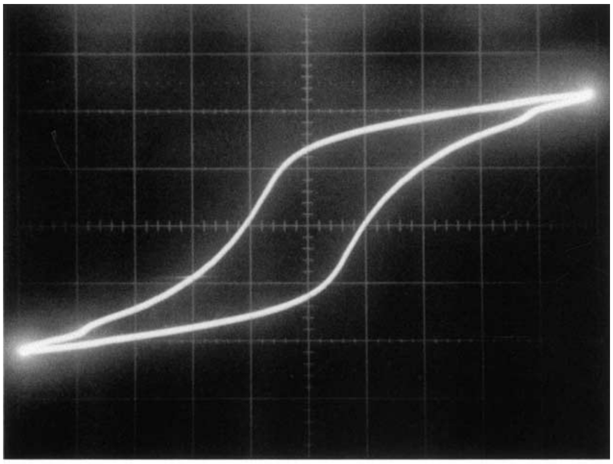

Fig. 4. P–E hysteresis loop of the PZT film shown in Fig. 2. P: 15.9 μC cm^{-2}/div., E: 90 kV cm^{-1}/div.

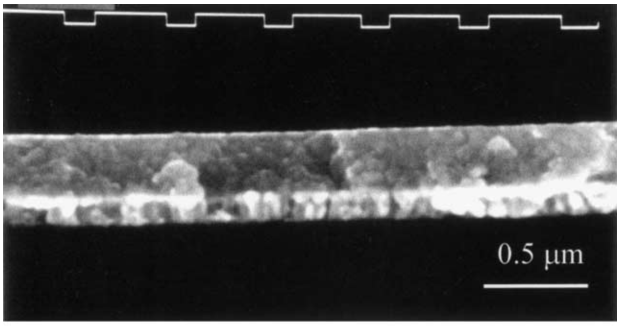

Fig. 5. SEM picture of the cross-section of the $BaTiO_3$ film deposited on a Pt/Ti/SiO_2/Si substrate via non-repetitive, single step deposition.

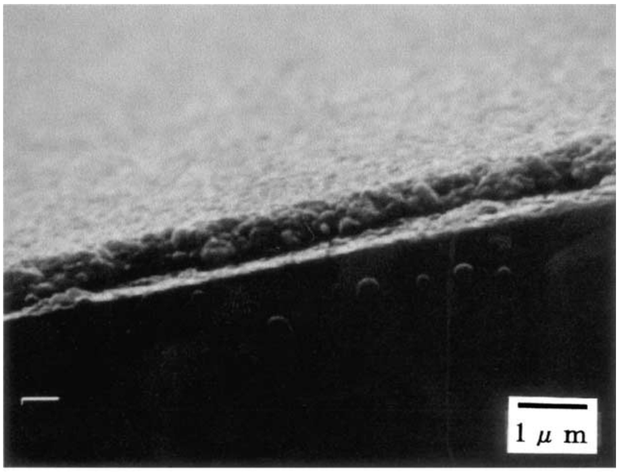

Fig. 6. SEM picture of the cross-section of the $BaBi_4Ti_4O_{15}$ film deposited on a $Pt/Ti/SiO_2/Si$ substrate via non-repetitive, single step deposition.

had a dielectric constant and loss tangent of 380 and 0.12, respectively at 1 kHz. The dielectric constant is higher than that of sintered polycrystalline $BaBi_4Ti_4O_{15}$ (220) reported by Kim et al.[15]

The gel films were found to be crystallized between 500 and 600 °C, where $BaBi_4Ti_4O_{15}$ phase appears as the primary phase. As has been experienced in PZT and $BaTiO_3$ film preparation, incorporation of PVP in precursor solutions allows formation of target complex oxides with ease, which is another benefit of PVP for fabricating ferroelectric thin films. PVP has C=O groups (Fig. 1), which can also coordinate metal atoms, offering homogeneity in metal atom distribution in sols and in gel films.

4. Summary

PZT, $BaTiO_3$ and $BaBi_4Ti_4O_{15}$ films were prepared on $Pt/Ti/SiO_2/Si$ substrates from solutions containing PVP, which were stable in viscosity over several hundred hours, via non-repetitive sol-gel spin-coating.

1. A single-phase PZT film as thick as 2.2 μm could be prepared. The film exhibited P–E hysteresis with P_r of 21 $\mu C\ cm^{-2}$ and E_c of 90 $kV\ cm^{-1}$. The dielectric constant was 370 and the loss tangent was 0.007 at 1 kHz.
2. A single-phase $BaTiO_3$ film 0.77 μm in thickness was obtained, having dielectric constant and loss tangent of 310 and 0.05, respectively, at 1 kHz.
3. A single-phase $BaBi_4Ti_4O_{15}$ film 0.40 μm in thickness could be obtained, showing dielectric constant and loss tangent of 380 and 0.12, respectively, at 1 kHz.

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