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Ferroelectric Lead Zirconate Titanate Films Prepared by Spray Pyrolysis of Carboxylate Solutions

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Abstract—Ferroelectric $PbTi_{0.6}Zr_{0.4}O_3$ films 0.5–1.5 μm in thickness were produced on platinum substrates by spray pyrolysis of carboxylate solutions. The optimized compositions of the precursor solutions, containing methacrylic acid and ethylene glycol, are stable under normal conditions, allow the annealing temperature to be reduced, and lead to higher quality film surfaces and large grains. The film exhibit the following electrical properties: T_C = 360–460°C, ε_{max} = 1750 at T_C, $\tan\delta$ = 0.02–0.1 at 1 kHz and room temperature, $P_{s_{max}}$ = 18 μC/cm^2, $P_{r_{max}}$ = 15 μC/cm^2 at 50 Hz, and E_c = 42–120 kV/cm.

INTRODUCTION

Lead zirconate titanate (PZT) ceramics are widely used in microelectronics, acousto- and optoelectronics, computer engineering, and sensors owing to their superior ferro-, piezo-, and pyroelectric properties [1]. PZT films have even greater potential for practical application, since they offer better sensor properties, faster response, and higher selectivity; their production requires less power; and they can readily be integrated into semiconductor technology [2]. Intensive research effort is being concentrated on the preparation of PZT films by chemical means, in particular, via precipitation from solution.

Mansour *et al.* [3, 4] prepared PZT films 0.8–1.0 μm in thickness by applying zirconium and titanium alkoxide solutions to a substrate; Pb was introduced as an acetate. Afanas'ev *et al.* [5] used a solution of $Zr(C_7H_{15}COO)_4$, $Pb(2\text{-}C_2H_5\text{-}C_5H_{10}COO)_2$, and $[(CH_3)_2Ti(\text{neo-}C_9H_{19}COO)_2]$ in xylene. Layers were deposited onto a rotating substrate. PZT films with Ti : Zr = 0.25–0.75 were also prepared by precipitation from solutions of lead 2-ethyl hexanoate, tetrabutyl titanate, and zirconium acetylacetonate in butanol [6]. To prevent the formation of the nonferroelectric, pyrochlore phase and compensate for the vaporization of lead oxide, an excess of Pb (2–12 mol %) was introduced into the precursor solution. La-doped PZT films were prepared by precipitation from a water–methanol (4 : 1 by weight) solution of zirconium and lanthanum acetates, titanium acetylacetonate, and lead basic acetate [3, 4, 7]. The substrates were slowly pulled from the solution. The solution pH was adjusted by aqueous ammonia or acetic acid. Acidic solutions were found to be more stable; the use of alkaline solutions led to gelation of the precipitate. Ozenbaz and Ergin [8], in order to prepare a true solution, used Ti, Zr, and Pb chlorides dissolved in urea; the pH of the solution was adjusted to 5.5 by controlled aluminum hydroxide additions. PZT films 1.1–1.2 μm in thickness were prepared by dipping substrates into the solution thus prepared, followed by slow pulling. De Veirman *et al.* [9] prepared $PbTi_{0.45}Zr_{0.55}O_3$ films up to 0.08 μm in thickness using, as a precursor solution, a mixture of $Pb(C_7H_{15}COO)_2$, $Ti(OBu\text{-}n)_4$, and $Zr(OPr\text{-}n)_4$ dissolved in isopropanol (30–50%). The solution was applied to the substrate by spin coating. PZT films with Ti : Zr = 52 : 48 were obtained from solutions of $Ti[(CH_3)_2CHO]_4$, $Zr(C_3H_7O)_4$, and $Pb(CH_3CO_2)_2$ in glacial acetic acid, distilled water, and propanol [10]. The solutions were applied to the substrate by spin coating. The film thickness was ≃1 μm. Lemanov *et al.* [11] prepared PZT films from 0.2 M solutions of the methyl cellosolvates $Pb(OC_2H_2OCH_3)_2$, $Ti(OC_2H_2OCH_3)_4$, and $Zr(OC_2H_2OCH_3)_4$ with components in the ratio Pb : Ti : Zr = 1.05 : 0.52 : 0.48. The solution were prepared by anodic dissolution of Pb, Ti, and Zr in methyl cellosolve, followed by spin coating. Thus, despite the wide diversity of the precursors used, the carboxylate route has received insufficient attention. At the same time, carboxylate solutions are easy to prepare, stable in air under ordinary conditions, and relatively inexpensive. They require no complex equipment to prevent contact with moisture or oxygen. Earlier, the carboxylate route was used with success to prepare superconducting cuprate films [12, 13]. Besides, of the many techniques for applying solutions to substrates, spray pyrolysis, undeservingly seldom used at the moment, is the easiest to implement, offers high flexibility of the process, and appears to be commercially viable. The objective of this work was to develop and optimize a procedure for producing PZT films from carboxylate solutions.

EXPERIMENTAL

Preparation of the precursor solutions. We prepared solid solutions with Ti : Zr = 0.6 : 0.4. The starting reagents were lead acetate trihydrate, $Pb(CH_3COO)_2 \cdot 3H_2O$; titanium isopropoxide, $Ti(OC_3H_7)_4$; and zirconium acetylacetonate decahydrate, $Zr(C_5H_7O_2)_4 \cdot 10H_2O$. Isopropanol and hexane were dehydrated by standard techniques [14] and then distilled over Na in an argon atmosphere. Titanium tetrachloride was distilled at atmospheric pressure in argon. Acetic acid was dehydrated and purified by freezing, followed by atmospheric-pressure distillation. Methacrylic acid was purified by reduced-pressure distillation over a polymerization stabilizer (copper powder). $ZrOCl_2 \cdot 8H_2O$ was purified by recrystallization, since it readily dissolves in water but is poorly soluble in cold 25 to 30% hydrochloric acid. In this way, we were able to remove Al, Fe, Nb, Ta, and Ti impurities.

Titanium isopropoxide was synthesized by a standard technique in a dry argon flow. Isopropanol was placed in a flat-bottom, three-mouth flask fitted with a stirrer, thermometer, dropping funnel, and refluxer with a T-joint for introducing and removing argon. Next, an appropriate amount of Na metal was added with heating, until complete dissolution, and titanium tetrachloride was introduced through a dropping funnel. As a result, we obtained a sodium chloride precipitate in an alcoholic medium.

The titanium alkoxide was separated from the reaction mixture by threefold extraction by hexane, followed by centrifugation. The liquid phases were poured together and distilled. Next, hexane and isopropanol were distilled off consecutively. Titanium isopropoxide was isolated by vacuum distillation with a yield of 59.7%.

To obtain zirconium acetylacetonate, zirconium oxychloride recrystallized from a chloride solution was dissolved in distilled water. After cooling, the solution was mixed with a 10% solution of acetylacetone in sodium carbonate, which was preliminary cooled and filtered. The resulting crystalline $Zr(C_3H_7O_2)_4 \cdot 10H_2O$ precipitate was collected on a filter and washed with distilled ice water. After dissolving zirconium acetylacetone in benzene and separating insoluble zirconium oxychloride by filtering, zirconium acetylacetonate was precipitated by petroleum ether with a yield of 53%.

Three types of precursor solutions were used. Solution A was prepared using isopropanol, distilled water, and acetic acid as solvents. Solution B was prepared by adding ethylene glycol to solution A. Solution C contained methacrylic acid instead of glacial acetic acid. The three solutions were homogeneous, transparent, and stable under normal conditions and wetted the substrates (polished Pt plates 12 × 4 mm in size, rinsed in extrapure-grade hexane and distilled water).

Spray coating. The precursor solutions were diluted with the solvents indicated above to a concentration of 2–4 g/l. Next, one of the solutions was introduced into an atomizer, propelled by compressed air (0.5 MPa), and directed through a nozzle onto a preheated substrate, situated 3–5 mm away from the outlet. The flow rate of air was 5–6 l/min, and the ejection velocity was 80–100 m/s. The consumption of the solution was 10–15 ml/h. Large drops (50–100 μm) were trapped and brought back to the atomizer. Also, large drops were prevented from reaching the substrate by the bent outlet tube, where the aerosol flow changed direction by 45°, so that the largest drops deposited on the wall. On the preheated substrate, part of the solvent vaporized, and the viscosity of the solution increased considerably. Each layer was deposited for 30 min; then, the deposit was dried at 350°C for 20 min, and the next layer was deposited. After the desired thickness was attained, the film was dried at 350°C for 4–8 h. As a result, the metalorganic precursors fully decomposed, and a dense layer consisting of fine-particle Pb, Ti, and Zr oxides was formed. This layer was then heat-treated at a high temperature. In this way, we prepared 18 films (Table 1).

Annealing conditions. The films were annealed in a Nabertherm L3/S furnace under a controlled temperature program (±1°C). A typical annealing schedule included heating to t_1 for time τ_1, holding at t_1 for time τ_2, heating to t_2 for time τ_3, holding at t_2 for time τ_4, heating to t_3 for time τ_5, holding at t_3 for time τ_6, and furnace-cooling. The annealing parameters were as follows:

$$\text{Nos. 1–6}\left\{\begin{array}{lll} t_1 = 350°\text{C} & \tau_1 = 1\text{ h} & \tau_2 = 1\text{ h} \\ t_2 = 650°\text{C} & \tau_3 = 2\text{ h} & \tau_4 = 4\text{ h} \end{array}\right.$$

$$\text{Nos. 7–12}\left\{\begin{array}{lll} t_1 = 350°\text{C} & \tau_1 = 1\text{ h} & \tau_2 = 3\text{ h} \\ t_2 = 750°\text{C} & \tau_3 = 5.3\text{ h} & \tau_4 = 1\text{ h} \end{array}\right.$$

$$\text{Nos. 13–18}\left\{\begin{array}{lll} t_1 = 350°\text{C} & \tau_1 = 5\text{ h} & \tau_2 = 4\text{ h} \\ t_2 = 750°\text{C} & \tau_3 = 5\text{ h} & \tau_4 = 1\text{ h} \\ t_3 = 850°\text{C} & \tau_5 = 4.5\text{ h} & \tau_6 = 1\text{ h} \end{array}\right.$$

The heating rate was varied from 0.98 to 2.5°C/min. The cooling rate was 3°C/min (Table 1).

The flow chart of the process is shown in Fig. 1.

Characterization techniques. To examine the microstructure of the films and determine their thickness, we used secondary electron images obtained on a JSM-35 CF scanning electron microscope (SEM) equipped with a Link energy-dispersive x-ray microanalysis system (magnifications of up to 10000). Film thickness was determined on a transverse section. We used standard ZAF programs and special programs

Table 1. Deposition and heat-treatment conditions (cooling rate, 3°C/min)

Film no.	Solution	Solution concentration, g/l	Number of layers	τ, h*	t, °C × τ, h**	Heating rate, °C/min
					$t_2 \times \tau_4$	
1	A	4	7	4	650 × 4	2.5
2	A	2	3	4	650 × 4	2.5
3	B	4	5	4	650 × 4	2.5
4	B	2	3	4	650 × 4	2.5
5	C	4	4	4	650 × 4	2.5
6	C	2	3	4	650 × 4	2.5
					$t_2 \times \tau_4$	
7	A	4	7	6	750 × 1	1.25
8	A	2	3	6	750 × 1	1.25
9	B	4	6	6	750 × 1	1.25
10	B	2	4	6	750 × 1	1.25
11	C	4	5	6	750 × 1	1.25
12	C	2	3	6	750 × 1	1.25
					$t_3 \times \tau_6$	
13	A	4	7	8	850 × 1	0.98
14	A	2	3	8	850 × 1	0.98
15	B	4	5	8	850 × 1	0.98
16	B	2	3	8	850 × 1	0.98
17	C	4	5	8	850 × 1	0.98
18	C	2	4	8	850 × 1	0.98

Notes: Solution A: $Ti(OC_3H_7\text{-}i)_4$, $Zr(C_5H_7O_2)_4$, $Pb(CH_3COO)_2 \cdot 3H_2O$, CH_3COOH, $i\text{-}C_3H_7OH$, H_2O; solution B: $Ti(OC_3H_7\text{-}i)_4$, $Zr(C_5H_7O_2)_4$, $Pb(CH_3COO)_2 \cdot 3H_2O$, CH_3COOH, $i\text{-}C_3H_7OH$, H_2O, $OHCH_2CH_2OH$; solution C: $Ti(OC_3H_7\text{-}i)_4$, $Zr(C_5H_7O_2)_4$, $Pb(CH_3COO)_2 \cdot 3H_2O$, $CH_2{=}C(CH_3)COOH$, $i\text{-}C_3H_7OH$, H_2O.

* Duration of the final drying at 350°C.

** Conditions of the final anneal.

for thin layers on substrates. The accelerating voltage was from 10 to 20 kV. Concentrations were evaluated from the TiK_α, PbL_α, and ZrL_α signals. Phase composition was determined by x-ray diffraction (XRD) with a DRON-4-07 powder diffractometer (CuK_α radiation). Dielectric measurements were made on thin-film capacitors in which the substrate was a base electrode, and frontside electrodes 1 μm in thickness were deposited by vacuum evaporation (10^{-3} Pa) of Au from a tungsten boat through masks with 1-mm^2 holes. The capacitors were mounted in a holder fitted with point contacts aided with silver paste. In ac resistivity measurements, we used a Shch301-1 digital meter. The capacitance and loss tangent were measured with a U7-8 bridge (at 1 kHz, the voltage across the sample was 4.3 V). To measure the dielectric permittivity and loss tangent as functions of temperature, the sample was heated in a special furnace. The temperature was monitored by a Chromel–Alumel thermocouple. The heating rate was 8°C/min, and the cooling rate was 4–5°C/min. Dielectric hysteresis loop measurements were made with a Sawyer–Tower circuit. Oscilloscope traces were used to evaluate the spontaneous polarization P_s, remanent polarization P_r, and coercive field E_c.

EXPERIMENTAL RESULTS

Each of the 18 PZT films was characterized chemically, by XRD, and by SEM. The deviation from the nominal metals composition (Pb : Ti : Zr = 1 : 0.6 : 0.4) was within 6%. All of the films were x-ray pure and had a perovskite structure (Fig. 2). Most of the films had a

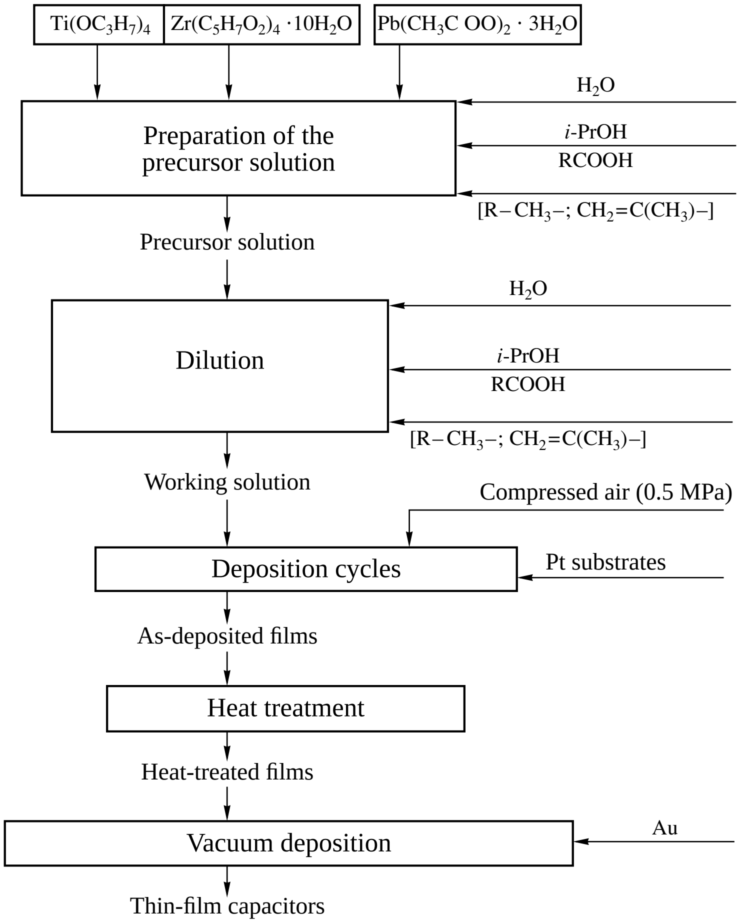

Fig. 1. Flow chart of PZT film fabrication on platinum substrates.

pseudocubic cell. In the XRD patterns of the films annealed at 850°C, the peaks at large angles were split, indicating a tetragonal distortion.

Most of the films were characterized by microstructural examination. Film 1 (solution A) showed heavy cracking. The surface of film 2 (solution A) was also cracky and porous. In films 3 and 4 (solution B), the average crack size was notably smaller, especially in film 4. Films 5 and 6 (solution C) had a smooth surface and a crystallite size of 0.2 and 0.6 μm, respectively. On the surface of film 8, prepared from solution A (2 g/l) and annealed at 750°C, we observed cracks; the film consisted of small roundish grains (average grain size of 0.6 μm). In film 14, prepared under similar conditions but annealed at 850°C, the average grain size was ≃2.2 μm, and the amount of cracking was much smaller. Films 10 and 16, both prepared from solution B but differing in annealing temperature, had smooth, crack-free surfaces, with an average grain size of ≃0.6 and ≃1.7 μm, respectively. Films 12 and 18, prepared from solution C and differing in annealing temperature, had smooth, crack-free surfaces and sharp grain boundaries, with an average grain size of ≃1.4 and ≃3.4 μm,

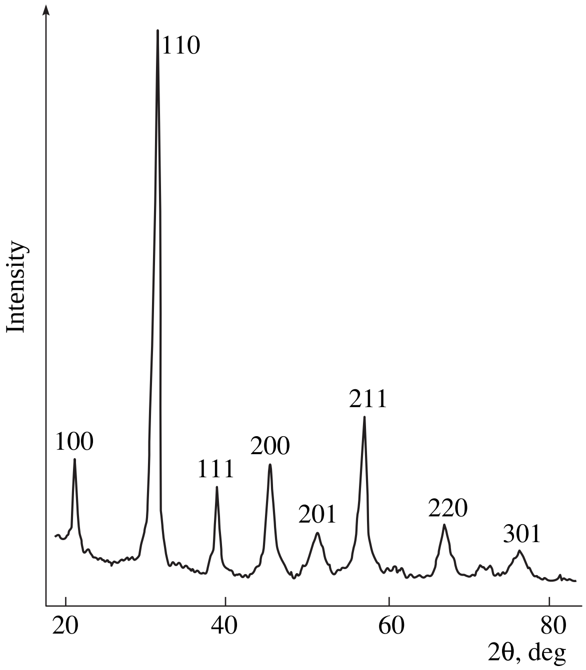

Fig. 2. XRD pattern from film 1.

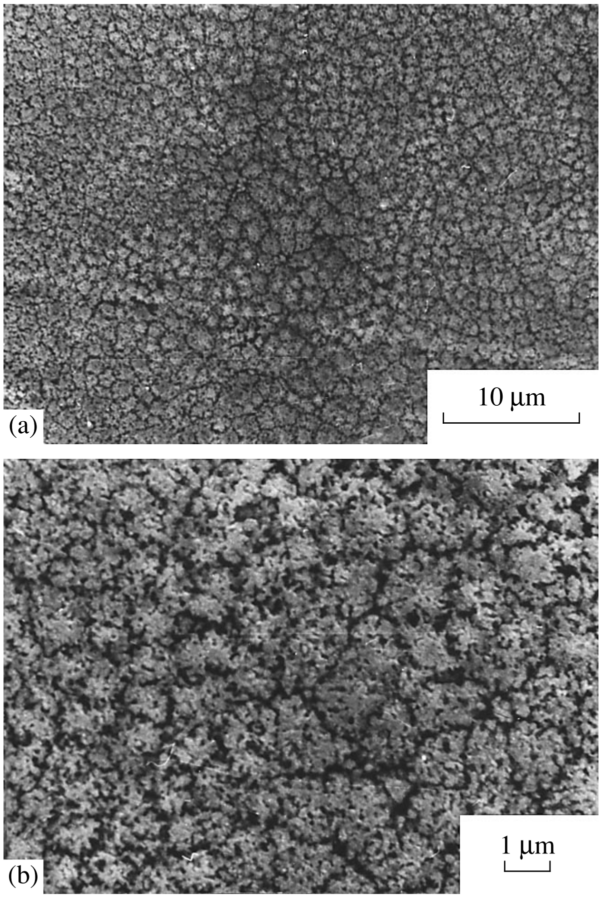

Fig. 3. SEM micrographs of films (a) 12 and (b) 18.

respectively (Fig. 3). The thickness, composition, and grain size of the films are listed in Table 2.

The electrical properties of six pore- and crack-free films are summarized in Figs. 4–6 and Table 3.

RESULTS AND DISCUSSION

Typical ε_{max} and P_s in our films are 1750 and 8–18 μC/cm^2, respectively, which is lower than in PZT ceramics, in which ε_{max} attains a few thousands and P_s attains 45 μC/cm^2 [10]. At the same time, our results agree with earlier data for PZT films (e.g., ε_{max} = 500–1500 and P_s = 2–30 μC/cm^2 in [3–11]). The absence of anomalies in the $\tan\delta(T)$ curves measured at 1 kHz is likely related to the low frequency. The values E_c = 42–120 kV/cm agree with those reported for PZT films (E_c = 60–200 kV/cm) but are higher than those for ceramics (≃17 kV/cm) [10]. These results suggest that the carboxylate process, when optimized further, will be capable of competing with other chemical routes. Additional advantages of carboxylates are their good solubility and the ability to form homogeneous mixtures, to wet substrates, and to decompose at relatively low temperatures without releasing metals or toxic gases. These properties are inherent in zirconium acetylacetonate, tetraisopropyl titanate, and lead acetate. The use of inorganic compounds, e.g., chlorides or nitrates, as starting reagents is ineffective, because of the high decomposition temperatures (>1000°C) and release of toxic nitrogen and chlorine oxides. To ensure full replacement of Cl ions in the preparation of tetraisopropyl titanate, we took sodium isopropoxide in excess of the stoichiometric value. The titanium alkoxide was separated by threefold extraction with hexane, followed by liquid–solid separation. The choice of hexane as a solvent is prompted by the fact that titanium alkoxides are readily soluble in hexane, and mixtures of hexane, isopropanol, and titanium alkoxides are easy to separate. The low viscosity and low surface tension of hexane are favorable for precipitate separation. Besides, hexane is nonhygroscopic and prevents hydrolysis of the titanium alkoxide, which was obtained in a yield of ≃60%, without titanium compounds with chlorine.

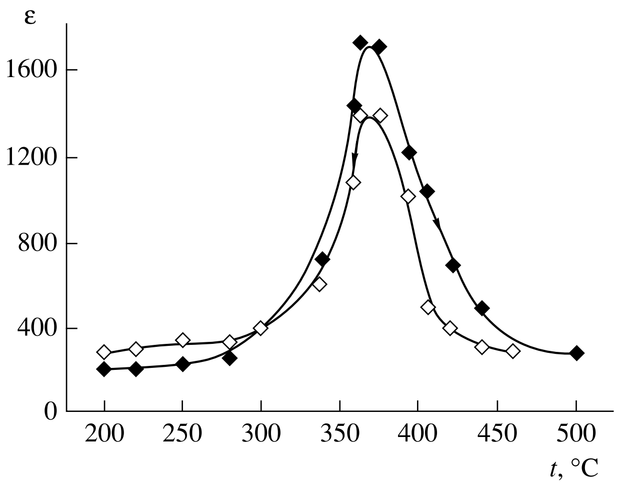

Fig. 4. Temperature dependences of 1-kHz permittivity for film 18.

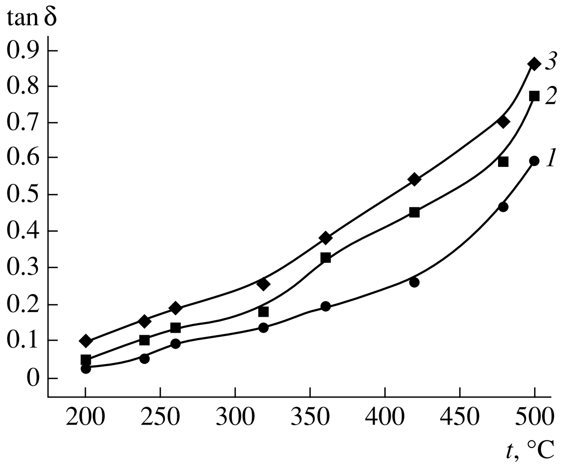

Fig. 5. Typical temperature dependences of tan δ at 1 kHz for the PZT films annealed at (*1*) 650, (*2*) 750, and (*3*) 850°C.

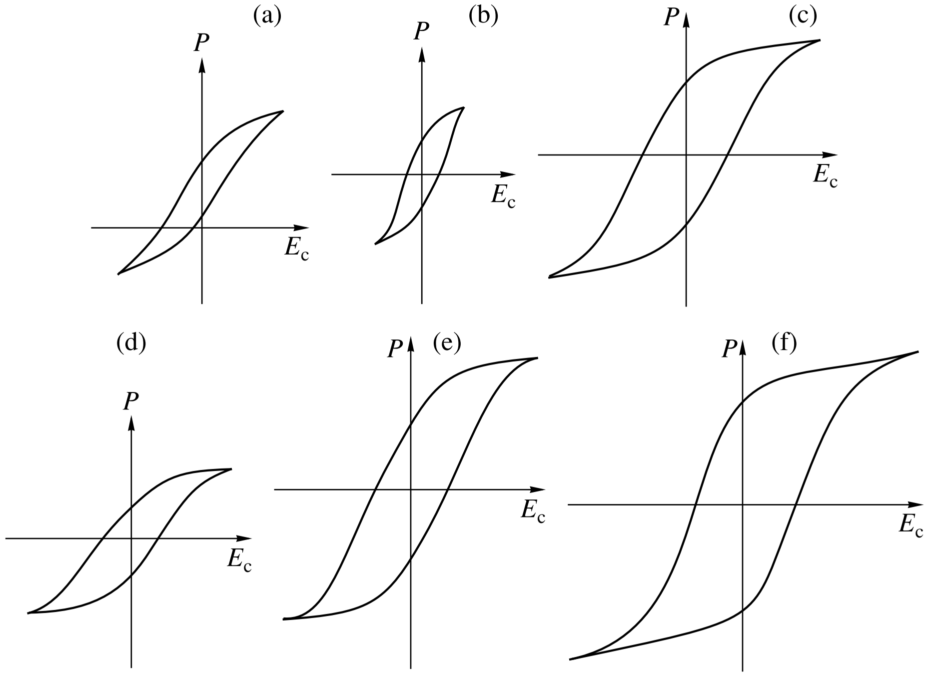

Fig. 6. Dielectric hysteresis loops at 50 Hz for films (a) 6, (b) 8, (c) 12, (d) 14, (e) 16, and (f) 18.

It was also found that, in preparing the precursor solution, the sequence in which the reagents are added is important. The solution of zirconium acetylacetonate in the corresponding carboxylic acid should be added to lead acetate dissolved in the appropriate amount of isopropanol with the addition of one to three drops of a carboxylic acid in order to prevent hydrolysis. Next, to this mixture is added titanium isopropoxide. Zirconium acetylacetonate should be introduced first because it reacts with the acid to form a nonhydrolyzable solution and prevents titanium isopropoxide from hydrolysis and condensation. If titanium isopropoxide is introduced first, it will react with the acid to form polytitanyl acetates, which will precipitate. Ethylene glycol should be added at the final stage, since it reacts with titanium alkoxides to form an insoluble precipitate. An important point in choosing the precursor solution for the spray pyrolysis process is its ability to be atomized by an air jet at a pressure of 0.5 MPa and room temperature. In view of this, the viscosity and surface tension of the substances for spray pyrolysis are of key importance. For this reason, we used isopropanol, water, acetic acid, and methacrylic acid as solvents that do not vaporize at room temperature (t_{vap} from 97 to 163°C). As a result, the precursor solutions were very stable under normal conditions and contained high levels of Pb, Ti, and Zr (45% in terms of oxides) and a minor amount of carbon, which reduced the probability of contamination with carboniferous compounds and prevented the formation of a reducing atmosphere in the course of pyrolysis.

The microstructure was found to be strongly correlated with the concentrations and compositions of the precursor solutions. At concentrations above 4 g/l, large cracks were formed, and spalling was observed. The

Table 2. Thickness *h*, chemical composition, and grain size *L* of PZT films (perovskite structure)

Film no.	*h*, mm	Ti : Zr molar ratio	*L*, μm
1	1.5	0.55 : 0.45	–
2	0.5	0.58 : 0.42	–
3	1.0	0.60 : 0.40	–
4	0.5	0.58 : 0.42	–
5	0.8	0.60 : 0.40	0.2
6	0.6	0.58 : 0.42	0.6
7	1.3	0.56 : 0.44	0.5
8	0.6	0.57 : 0.43	0.6
9	1.1	0.60 : 0.40	0.7
10	0.7	0.58 : 0.42	0.6
11	0.9	0.54 : 0.46	0.9
12	0.5	0.57 : 0.43	1.4
13	1.3	0.56 : 0.44	2.0
14	0.6	0.54 : 0.46	2.2
15	1.0	0.59 : 0.41	1.7
16	0.5	0.59 : 0.41	1.7
17	0.9	0.57 : 0.43	3.4
18	0.7	0.60 : 0.40	3.4

Table 3. Electrical properties of PZT films

Film no.	ε_{20}	ε_{T_C}	P_s, μC/cm^2	P_r, μC/cm^2	E_c, kV/cm
6	650	1225	8	5	42
8	650	1000	6	5	44
12	600	1350	8	5	120
14	250	1000	14	10	84
16	300	1450	13	10	120
18	250	1750	18	15	107

optimal concentration was 2 g/l. At this concentration, the films had smooth surfaces without pores or cracks. At lower concentrations, the microstructure does not improve, but the process takes more time, and the consumption of the precursor solution increases. The introduction of ethylene glycol raises the solution viscosity, inhibits vaporization of the solvent from the substrate, and notably improves the quality of the film surface. The presence of methacrylic acid reduces the mechanical stress in the deposited layer, which also favors the formation of pore- and crack-free films. The consecutive deposition of several layers helps obtain stress-free films uniform in thickness. Our experiments demonstrate that, all other factors being the same, the porosity and amount of cracking are lower in multilayer films.

The optimal substrate temperature in the course of deposition is 200°C, which ensures sufficiently high viscosity of the deposited solution and good adhesion to the substrate. The optimal temperature of the first stage of annealing is 350°C. At this temperature, the organic precursors fully decompose, without creating a reducing atmosphere. Since data on the optimal annealing temperature are not available in the literature, we carried out anneals at 650, 750, and 850°C—the most frequently reported temperatures; the heating rate was varied from 0.98 to 2.5°C/min. According to chemical analysis and XRD data, at these heating rates, lead vaporization and surface cracking are insignificant.

The crystallite size was found to depend not only on the annealing temperature but also on the compositions of the precursor solutions. For example, with the solution containing methacrylic acid, the grain size is $\simeq 0.6$ μm after annealing at 650°C, whereas, with acetic acid, this grain size is attained only by annealing at 750°C. All other factors being the same, the presence of methacrylic acid favors grain growth. The average grain size after annealing at 750°C is 0.6 μm in the film prepared with the use of acetic acid and 1.4 μm in the case of methacrylic acid. At 850°C, we obtain, respectively, 2.2 and 3.4 μm. Increasing the annealing temperature to 850°C improves the structural perfection of the films, and the pseudocubic structure gives way to the equilibrium, tetragonal structure.

CONCLUSION

PZT films with Ti : Zr = 0.6 : 0.4 and good ferroelectric properties were prepared by spray pyrolysis of carboxylate solutions. The perfection of the films was found to strongly depend on the composition and concentration of the precursor solutions and annealing conditions. The introduction of methacrylic acid and ethylene glycol into the precursor solution leads to smoother film surfaces, reduces the amount of cracking and porosity, and allows the annealing temperature to be reduced without an adverse effect on the properties of the films.

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