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Development of phases and texture in sol-gel derived lead zirconate titanate thin films prepared by three-step heat-treatment process

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Lead zirconate titanate (PZT) films were fabricated by the addition of 10 mol% excess Pb to the starting solution which was spin-coated onto Pt/Ti/SiO_2/Si substrates. The effect of film thickness on texture was investigated, and it is clear that the (100) texture gradually increases and the (111) texture decreases with increasing film thickness. A Pt_xPb intermetallic metastable phase was observed by X-ray diffraction, and it is found that the position of this peak shifted from 38.30° 2θ (d: 0.2348 nm) to 37.10° 2θ (d: 0.4213 nm) with increasing firing temperature from 350°C to 550°C. The (111) preferred orientation in the PZT film was promoted by the metastable Pt_xPb phase. The formation of the (100) texture of perovskite phase in the multilayer films was mainly attributed to the effects of both substrates and crystal growth rates which depend on the crystal orientation. *© 2000 Kluwer Academic Publishers*

1. Introduction

Lead zirconate titanate ($Pb(Zr_XTi_{1-X})O_3$: PZT) films have received great interest because of their ferroelectric, pyroelectric and piezoelectric properties. PZT films are currently widely studied from the viewpoints of their manufacture and application to micro electromechanical system (MEMS) [1–5]. Many thin film fabrication techniques, such as sputtering [6], laser ablation [7], metal organic deposition [8] and the sol-gel process [5], have been used to fabricate ferroelectric thin films on various substrates. The sol-gel process yields a high purity, large deposition area, enables easy composition control, and is one of the most promising techniques for ferroelectric thin film fabrication.

In our previous work [5], crack-free PZT films of 3 μm thickness were fabricated using sol-gel spin-coating onto Pt/Ti/SiO_2/Si substrates. The well-crystallized perovskite phase with (100) texture was obtained using the heat treatment for drying at 120°C, for pyrolysis at 300°C and for crystallization at 600°C. However, the formation mechanism of the (100) texture corresponding to this heat-treatment process is not fully understood. Understanding the mechanisms involved in the nucleation and growth of the perovskite phase will be of vital importance in optimizing the sol-gel processing conditions. There have been some recent studies on the nucleation and growth of the perovskite phase of this material [9–11]. Tuttle *et al.* [9] proposed that the perovskite phase nucleates from Pt crystallites or from hillocks protruding from the bottom Pt layers. Chen and Chen [10] recently reported an intermetallic $Pt_{5-7}Pb$ transient phase that forms epitaxially on the Pt (111) substrate in their metal organic deposition (MOD) process. Although this intermediate interfacial phase is only a transient phase, it leads to the selection of the PZT variant because of the good lattice matching between itself and the PZT variant. Huang *et al.* [11] also observed that the Pt_xPb phase was formed in the Pt electrode but they report that the intermetallic phase was actually Pt_3Pb, and they suggest that the (111) orientation film was promoted by the formation of the metastable Pt_3Pb phase.

In this work, the development of phases and texture in multilayer PZT films during heat-treatment were investigated. The PZT films were fabricated with the addition of 10 mol% excess Pb to the starting solution which was spin-coated onto Pt/Ti/SiO_2/Si substrates. Crystalline phases as well as preferred orientations in the PZT films were investigated using X-ray diffraction analysis (XRD), and the film microstructure was studied by transmission electron microscopy (TEM). Based on these results, the mechanism of the development of phases and texture in the multilayer PZT films was discussed.

2. Experimental procedure

The precursor solution was prepared from lead acetate [$Pb(CH_3COO)_2$], zirconium-*n*-propoxide [$Zr(OCH_2CH_2CH_3)_4$] and titanium tetraisopropoxide [$Ti((CH_3)_2CHO)_4$]. 2-Propanol [$(CH_3)_2CHOH$] was used as the solvent. Each concentration was controlled to the ratio of Pb : Ti : Zr = 1.1 : 0.47 : 0.53. Lead acetate (5.362 g) was dissolved in acetic acid [CH_3COOH] (3.5 ml) on heating at 70°C for 20 min. The molarity of the lead acetate solution was about 3 M. The solution was cooled to room temperature, and the solutions of zirconium-*n*-propoxide (3.720 g) and titanium tetraisopropoxide (2.004 g) were added. After mixing for 40 min in ultrasonic cleaner, the water (3 ml), acetic acid (5 ml), 2-Propanal (10 ml) and ethylene glycol (0.5 ml) were added. The final concentration of the solution was adjusted to 0.4 M $Pb_{1.1}(Zr_{0.53}Ti_{0.47})O_3$ by the addition of 2-Propanal. Details of the synthesis of the precursor solution have been described in our prior publication [5].

PZT films were fabricated onto $Pt(111)/Ti/SiO_2/Si$ substrates using spin-coating at 2600 rpm for 20 s and 4000 rpm for 40 s. These substrates were prepared by sputtering 0.05 μm of titanium onto an oxidized (1.8 μm of SiO_2) silicon substrate, and then sputtering 0.15 μm of platinum. Before coating, the precursor solution was passed through 0.45 μm nylon filters. After the deposition process, the coated films were dried at 120°C for 10 min, pyrolyzed at 300°C for 30 min and then finally annealed at 600°C for 30 min. In order to decrease the influence of thermal stress during the heat-treatment process, the samples were continuously heated in an identical furnace. This coating and heat-treatment process was repeated from 1 to 15 cycles, and the effect of the thickness on the preferred orientation of the films was investigated. In order to investigate the effect of firing temperature for pyrolysis on the formation of preferred orientations, the single-layer PZT films were fired by the direct insertion method at several temperatures ranging from 300°C to 600°C for 20 min, and their preferred orientations was examined. The development of the phase and texture in the single-layer PZT films with the holding times at 550°C was also investigated.

Crystalline structures and crystal orientations of the obtained PZT films were examined using an X-ray diffractometer (Rigaku RINT2000) with Cu K_α radiation ($\lambda = 1.5418$ Å). The surface and cross-sectional fracture morphology of the PZT films were observed using a scanning electron microscope (JSM-6400F). The microstructures of the films were studied by transmission electron microscopy (H-9000UHR).

3. Results and discussion

Fig. 1 shows the XRD patterns of the PZT films fabricated with different coating cycles. All films were dried at 120°C for 10 min, pyrolyzed at 300°C for 30 min and then finally annealed at 600°C for 30 min after the coating in each cycle. The patterns show that all the films consist of mainly the perovskite phase without the pyrochlore phase and the grain orientations of the films strongly depend on the coating cycles. The films subjected to five coating cycles show (100) and (111) preferred orientations. However, the diffraction intensity from the (111) planes significantly decreases and the (100) peak increases with increasing the coating cycle from ten cycles (Fig. 1d and e). The relative intensity for (100) and (111) planes can be computed by $I_{(100)}$ (or $I_{(111)}$)$/[I_{(100)} + I_{(111)}]$, where $I_{(100)}$ and $I_{(111)}$ are the measured X-ray intensities of the (100) and (111) planes, respectively. As shown in Table I, it is clear that the (100) texture gradually increases and the (111) texture decreases with increasing film thickness.

TABLE I Relative intensity of the (100) and (111) plane for the PZT films with different coating cycles

Coating cycles	1	2	3	5	10	15
$I_{(100)}/[I_{(100)} + I_{(111)}]$	0.591	0.556	0.568	0.603	0.852	0.830
$I_{(111)}/[I_{(100)} + I_{(111)}]$	0.409	0.444	0.432	0.397	0.148	0.170

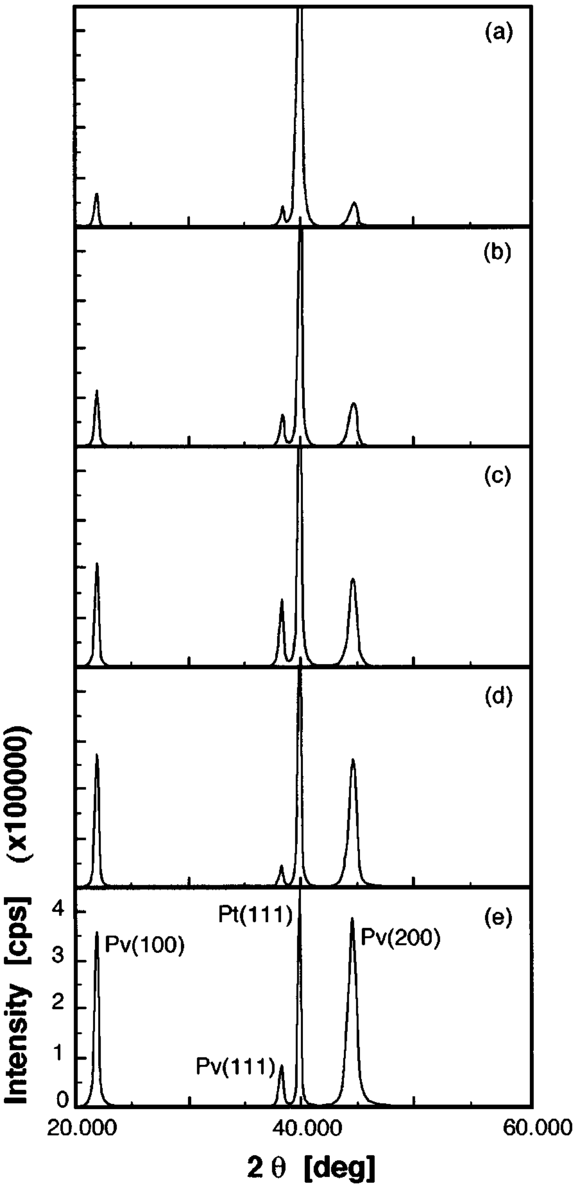

Figure 1 XRD patterns of PZT films with (a) 1, (b) 3, (c) 5, (d) 10, and (e) 15 coating cycles, which were dried at 120°C for 10 min, 300°C for 30 min and then annealed at 600°C for 30 min after the coating at each cycle. Pv: perovskite phase.

A TEM image of the cross-section of the films is shown in Fig. 2. It can be seen that the film has a columnar structure and no boundary between these layers can be observed. This suggests that the nucleation of the perovskite phase was from the PZT/Pt film interface and the subsequent coated layer crystallization was influenced by the surface of the underlying layer.

The formation of the (100) texture of the perovskite phase in the multilayer films may be mainly attributed to the effects of both substrates (Pt(111) or PZT layer) and on the crystal growth rate which is dependent on the crystal orientation. Namely, due to the effect of the

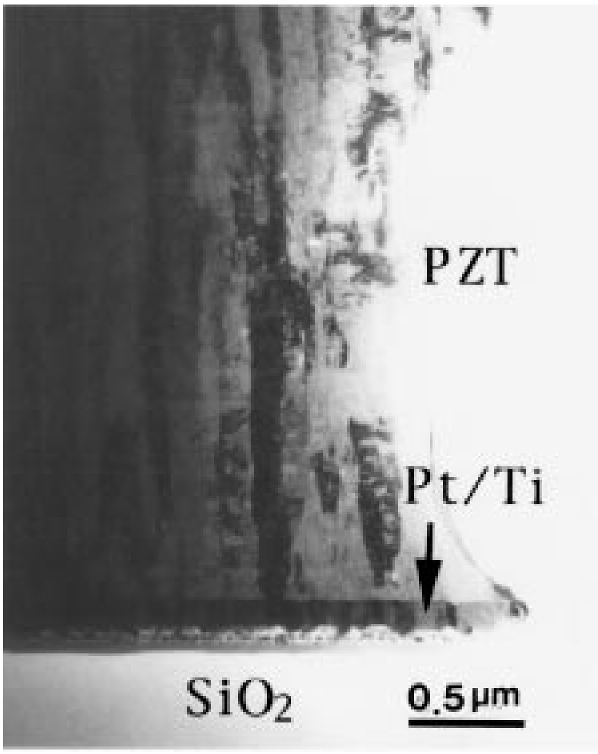

Figure 2 Cross-section a TEM image of the PZT film with 23 coating cycles, which were dried at 120°C for 10 min, 300°C for 30 min and then finally annealed at 600°C for 30 min after the coating at each cycle.

Pt substrate, the first film possesses (100) and (111) orientations, and the (100) crystals whose growth rates are higher than those of the (111) crystals, grow preferentially, leading to (100)-orientated multilayer films.

In order to investigate the effect of firing temperature for pyrolysis on the development of phases, the single-layer PZT films fired at temperatures ranging from 300°C to 600°C for 20 min using a direct insertion method were investigated. The phase development for the films determined by XRD is tabulated in Fig. 3 as a function of firing temperature. The sample fired at 300°C exhibits a typical amorphous pattern. A peak at 38.30° 2θ ($d = 0.2348$ nm) was first observed in the film after firing at 350°C (see Fig. 3b). The peak initially increased with firing temperature, then decreased until it finally disappeared after 600°C and had the maximum intensity at a firing temperature of approximately 450°C (see Fig. 3d). It was found that the peak positions shifted from 38.30° 2θ ($d = 0.2348$ nm) to 37.10° 2θ ($d = 0.2421$ nm) with increasing firing temperature ranging from 350°C to 550°C (Table II). Chen and Chen [10] determined that an epitaxial $Pt_{5-7}Pb$ phase was formed in the early stage of pyrolysis of PZT films and the highly (111) textured Pt_xPb phase produced only one reflection at 38.50° 2θ ($d = 0.234$ nm). Huang *et al*. [11] indicated that the peak at $d = 0.234$ nm initially increased with annealing time, then decreased until it finally disappeared after about 780 s at 440°C and the intermetallic phase was actually Pt_3Pb. We too believe metastable phase is Pt_xPb, but we can't identify whether it is Pt_3Pb or $Pt_{5-7}Pb$. Our results show that the d-spacing of the metastable phase vary with increasing firing temperature. This may be attributed to the fact that the Pt/Pb ratio varies with firing temperature. However, in order to clarify this point, further investigation would be required.

TABLE II Variation of d-spacing of the metastable intermetallic phase with increasing firing temperature ranging from 350°C to 600°C

Firing temperature (°C)	350	400	450	475	500	525	550
d(nm)	0.2348	0.2366	0.2372	0.2378	0.2396	0.2415	0.2421
2θ	38.30	38.00	37.90	37.80	37.50	37.20	37.10

The pyrochlore phase appeared at 475°C, and was clearly observed in the film after firing at 500°C (see Fig. 3e and f). It was observed that the intensity of the pyrochlore phase was almost constant until a firing temperature of up to 600°C. These results mean that the pyrochlore phase is stable under 600°C.

After firing at 550°C the peaks for the (100) and (111) planes of the perovskite phase were clearly observed. However, significant amounts of the pyrochlore phase and the metastable phase were observed. The peaks of the (100) and (111) planes of the perovskite phase were already predominant after firing at 600°C, while the pyrochlore and metastable phases were markedly decreased. It is clear that these films formed the complete perovskite phase at 600°C.

The development of phases and preferred orientation in the single-layer PZT films with the holding times at 550°C were also investigated. Fig. 4 shows the XRD patterns of PZT films heat-treated at 550°C for different holding times. For the film heat-treated for 5 min it is seen that the pyrochlore phase and the metastable phase at 37.80° 2θ ($d = 0.2378$ nm) appear simultaneously. When the holding time reaches 1 hour, the peak of the metastable phase at 37.10° 2θ ($d = 0.2421$ nm) decreases, and the peak of (111) planes of the perovskite phase is clearly observable. Then the metastable phase disappears and the peaks of (111) planes of the perovskite phase are dominant, when the holding time reaches 3 hour. This indicates that the generation of crystals of (111) orientation in the perovskite phase are related to the metastable phase. Chen and Chen [10] suggest that the (111) orientation follows that $Pt_{5-7}Pb$ (111), because of this, a good matching of d-spacing is obtained between Pt ($a_0 = 0.3922$ nm), $Pt_{5-7}Pb$($a_0 = 0.4050$ nm) and PZT ($a_0 = 0.4077$ nm). Huang *et al*. [11] also believe that the metastable phase Pt_3Pb acts as a lattice-matching buffer layer between Pt and PZT. Our results show that the d-spacing and peak intensity of the metastable phase vary with firing temperature for pyrolysis. This means that the firing temperature for pyrolysis significantly affects the texture of PZT films during the heat treatment.

On the other hand, the peaks of the (100) planes were observed in the early stage of crystallization of the perovskite phase. Chen and Chen [10] proposed that the (100) orientation is formed on the PbO buffer layer which can occur above a firing temperature of 300°C in their MOD process. It has also been suggested that the (100) orientation of PZT crystals, which minimize surface energy, is the energetically favored growth direction [12]. In our work, the second of these mechanisms

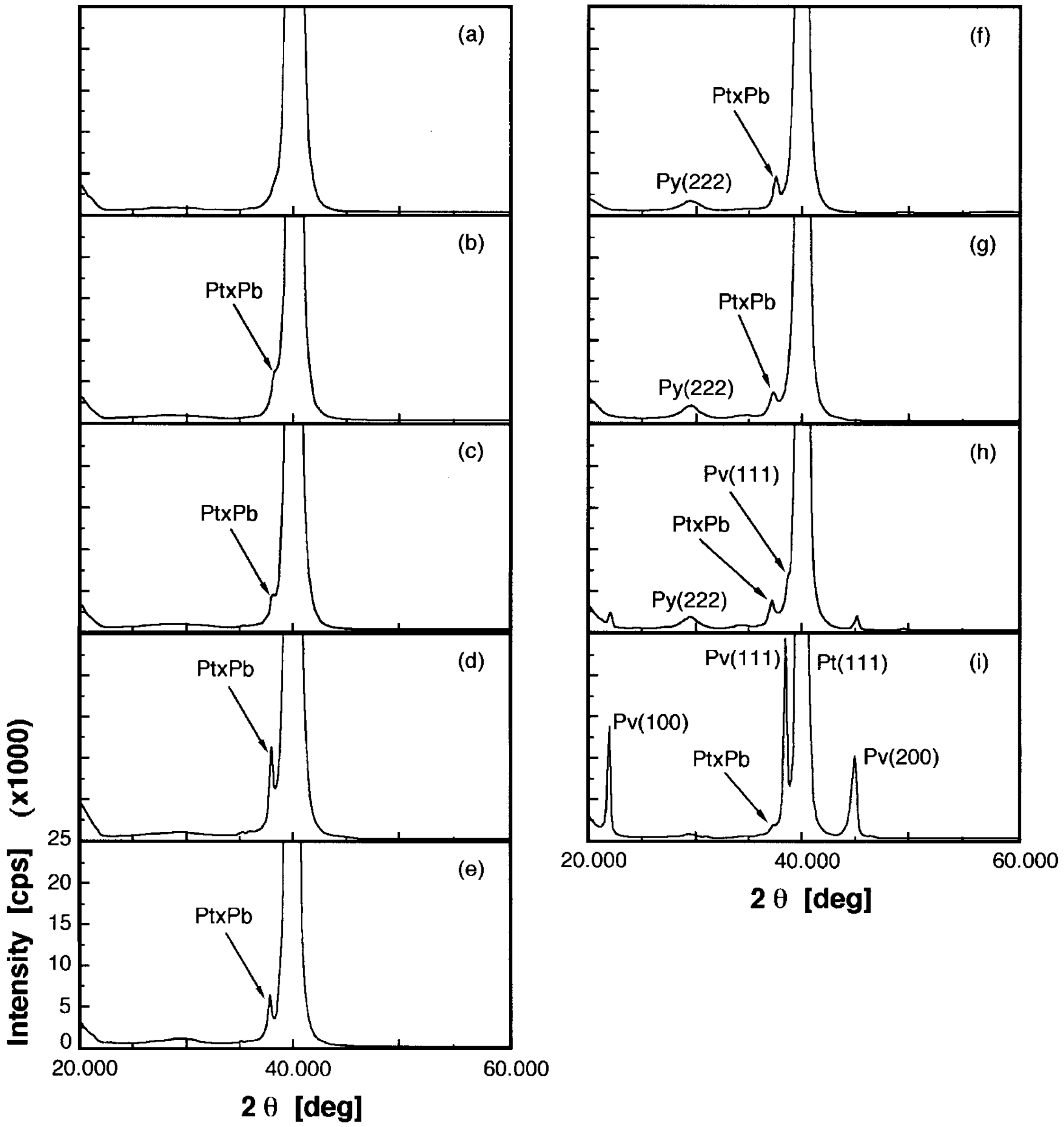

Figure 3 XRD patterns of single-layer PZT films fired at (a) 300°C, (b) 350°C, (c) 400°C, (d) 450°C, (e) 475°C, (f) 500°C, (g) 525°C, (h) 550°C, and (i) 600°C for 20 min. Pv: perovskite phase; Py: pyrochlore phase.

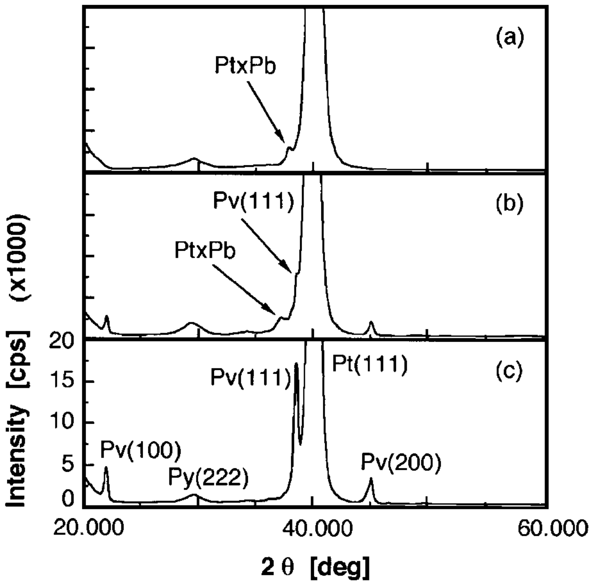

Figure 4 XRD patterns of single-layer PZT films annealed at 550°C for (a) 5 min, (b) 60 min, and (c) 180 min. Pv: perovskite phase; Py: pyrochlore phase.

is supported, because of this, the XRD patterns of PbO can't be observed in all the firing from 300°C to 600°C and the (100) texture was gradually enhanced and the (111) texture decreased with increasing film thickness (Fig. 1).

4. Conclusions

PZT thin films were fabricated onto Pt/Ti/SiO_2/Si substrates using the sol-gel process. The well-crystallized perovskite phase with (100) preferred orientation was obtained using the heat treatment for drying at 120°C, for pyrolysis at 300°C and for crystallization at 600°C. It is evident that the (100) texture gradually increases and the (111) texture decreases with increasing film thickness. A Pt_xPb intermetallic metastable phase was observed by X-ray diffraction upon firing for pyrolysis at temperatures ranging from 350°C to 600°C for 20 min, and it is found that this peak shifted from 38.30° 2θ ($d = 0.2348$ nm) to 37.10° 2θ ($d = 0.4213$ nm) with increasing firing temperature ranging from 350°C to 550°C. The (111) preferred orientation in the PZT film was promoted by the formation of the metastable Pt_xPb phase. The formation of the (100) texture of the perovskite phase in the multilayer films was attributed to the effects of the substrate and crystal growth rates which depended on the crystal orientation.

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