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Investigation of the drying temperature dependence of the orientation in sol–gel processed PZT thin films

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The crystal orientations of lead zirconate titanate (PZT) thin films have been investigated by using various drying temperatures in the sol–gel process. The films were dried at different temperatures between 310 and 350 °C for pyrolysis and then were heat treated at 650 °C using rapid thermal annealing (RTA). TG/DTA and FTIR spectroscopy were used to detect the remnants of organic materials in the thin films prior to the final heat treatment. In order to examine the relationship between the film orientation and the remaining organic materials for the prior and final heat treatment, the films were fabricated with different coating cycles and dried for different holding times and then annealed at 650 °C. The preferred orientations were investigated using X-ray diffraction.

1. Introduction

Ferroelectric P(L)ZT thin films have potential applications for integrated devices such as ferroelectric memory, infrared sensors and microactuators [1–4]. Since the electrical properties of P(L)ZT thin films are strongly dependent on the Zr/Ti composition ratio, the control of composition is a major obstacle in their application. The sol–gel process which provides relatively easy composition control is widely used to fabricate ferroelectric P(L)ZT thin films for device applications. On the other hand, the electrical properties of P(L)ZT thin films also depend on their orientations, so that it is important to control the crystal orientation during the film fabrication process. In general, compared to polycrystalline P(L)ZT thin films, oriented P(L)ZT thin films have the following merits (i) low operating voltage, (ii) high Ps and Pr value on the *P–E* hysteresis and (iii) high quality electrical properties. For example, (0 0 1) oriented PLT thin films have a higher pyroelectric coefficient than films having other orientations or random orientation, so that (0 0 1) oriented films have been used as elements of IR detectors.

In this work, (1 0 0), (1 1 1) and mixed oriented PZT thin films were fabricated on Pt/Ti/glass substrates using a sol–gel method, and the drying temperature and the holding time effects on the film orientation were investigated. A possible mechanism for the formation of the preferred orientation was proposed and speculated upon based on the observations made in this study.

2. Experimental procedure

The Pt and Ti bottom electrodes were deposited on Corning 7059 glass by rf (radio frequency) magnetron sputtering at ambient temperature with a gas pressure of 0.32 Pa and argon atmosphere. Lead acetate trihydrate, zirconium *n*-propoxide, and titanium isopropoxide were used as starting materials for preparing the 0.4 M $Pb(Zr_{0.52}Ti_{0.48})O_3$ solutions as described by Kim *et al.* [5]. A portion of the PZT solution was dried at 70 °C for 3 h for the analysis of the thermal annealing behaviour of the resulting powder. Thermogravimetric (TG) and differential thermal analyses (DTA) were performed in air atmospheres at a heating rate of 10 °C min^{-1}. For temperature programmed desorption (TPD) measurements, 300 mg of the dry powder was inserted into a quartz TPD cell which was heated up to 600 °C at a rate of 10 °C min^{-1}. Helium was used as a carrier gas to keep the interior of the TPD cell as an inert atmosphere. Gaseous species produced during the annealing process were monitored by a quadrupole mass spectrometer (VG, SX300). Chemical bond configurations of films as a function of the drying temperature were investigated using a Fourier-transform infrared (FTIR) spectrometer (Bomem, DA8).

The thin films were fabricated by spin-coating at 3000 r.p.m. for 30 s onto Pt/Ti/Corning 7059 glass. After the deposition process, the coated film was dried at different temperatures (310–350 °C) for different holding times (5, 30 and 60 min). The coated films were finally annealed at the same temperature of

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650 °C for 1 min in air using rapid thermal annealing (RTA) with a heating rate of about 60 °C s^{-1}. The crystal orientation of the obtained PZT thin films were analysed by X-ray diffraction (XRD) using CuK$_\alpha$ radiation.

3. Results and discussion

Fig. 1 shows XRD patterns of the PZT thin films dried at different temperatures for the pyrolysis and then finally annealed at the same temperature of 650 °C for 1 min using RTA. All the films consisted of the perovskite PZT phase with no pyrochlore phase. Since the heating rate of the rapid thermal annealing (RTA) is very fast, the temperature of the film passes rapidly through the region in which the pyrochlore phase is stable and hence able to nucleate. Therefore the RTA enhances the nucleation of the perovskite phase and inhibits that of the pyrochlore phase. The film dried at 350 °C (Fig. 1c) shows (1 0 0) preferred orientation, whereas that at 330 °C shows (1 1 1) preferred orientation. The XRD pattern of the film dried at 310 °C shows (1 0 0), (1 1 0) and (1 1 1) peaks (Fig. 1a). The relative intensity of the (1 1 1) peak is high in Fig. 1a compared to that in the standard pattern of polycrystalline PZT powder in which the (1 1 0) peak is the most strong, which may indicate that the film dried at 310 °C also showed some (1 1 1) preferred orientation. The drying temperature for pyrolysis affects the orientation of the PZT films. Our previous work [6] and Tani *et al.* [7] reported that the Pt–Ti intermetallic compounds on the boundary between Pt and PZT films served as the perovskite nucleation site as well as the preferred growth of (1 1 1) perovskite phase during the heat treatment for crystallization [6, 7]. On the other hand, a (1 0 0) preferred orientation can be attributed to self-textured F-face growth of the lowest surface-energy face [7]. This report, however, does not give further explanations about the cause of the change in the orientation of the film with the drying temperature. The following investigations will explain a possible cause for the change in the orientation with drying temperatures for pyrolysis.

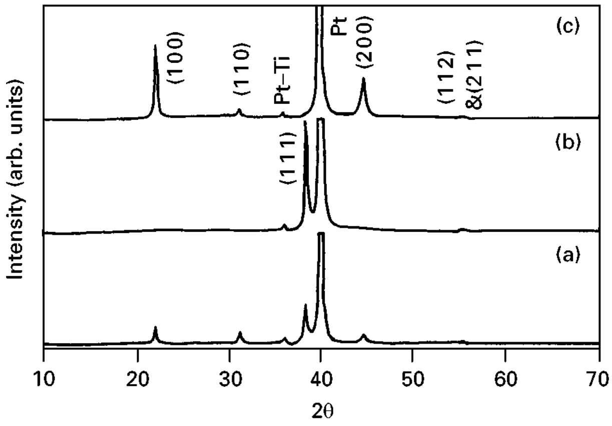

Figure 1 XRD patterns of the PZT(52/48) films dried at (a) 310 °C, (b) 330 °C and (c) 350 °C and then finally heat treated at the same temperature of 650 °C using RTA for 1 min.

Fig. 2 shows the DTA/TG curves of the PZT sol–gel powder dried from solution. The powder lost about 20% of its initial weight during the heat treatment up to 600 °C. A remarkable weight loss is found at around 300 °C. This may be due to the vaporization of the organics which were observed from the TPD spectra of the sol–gel powder (Fig. 3). The other DTA peak occurs around 510 °C, which seems to be due to the thermal decomposition of organic residue and the crystallization of dry PZT gel powder. From these results, we found that the dried PZT films still had organic residue at around 300 °C.

Mass spectroscopy is a good method to identify the species evolved during the heat treatment process.

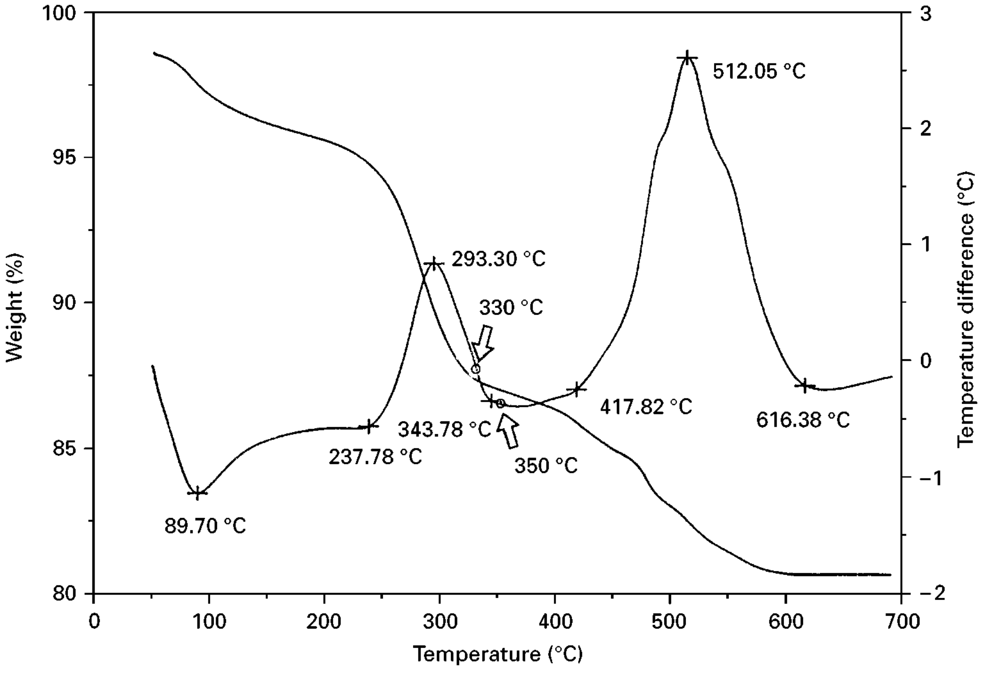

Figure 2 TG—DTA patterns of the powder dried at 70 °C.

Fig. 3 shows the TPD spectra of a powder dried from solution. A large amount of CO_2, CO, H_2O and OH was detected between 270 and 400 °C. The CO_2 and H_2O could be formed by the reaction between the 2-metoxyethanol and lead acetate as follows. One alkoxy group replaces one of the acetate groups [8].

$$Pb(OAc)_2 + ROH \;=\; Pb(OAc)(OR) + AcOH, \quad (1)$$

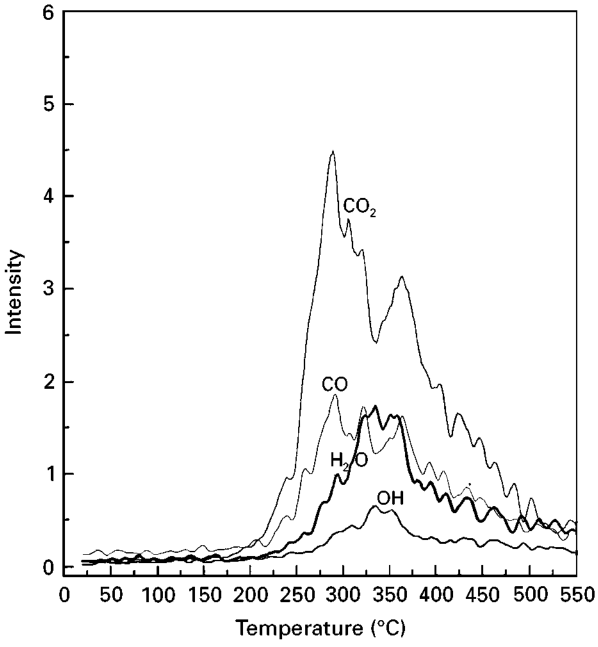

Figure 3 TPD curve of powder dried at 70 °C.

where $R = –CH_2CH_2OCH_3$, and $Ac = CH_3CO–$. Also, the produced (AcOH) reacts with the solvent, 2-methoxyethanol, as follows:

$$AcOH + ROH \;=\; AcOR + H_2O, \quad (2)$$

releasing a certain amount of free water into the system. Based on these results, the weight loss in Fig. 2 between 200 and 500 °C could be due to the decomposition of CO_2, CO, H_2O and OH in the precursors.

Fig. 4 shows the FTIR spectra of PZT films dried at different temperatures. The peak at about 1340 cm^{-1} represents the C–H bond. Generally, the peaks in the ranges of 1360 $\sim$ 1450 and 1540 $\sim$ 1650 cm^{-1} represent the symmetric and asymmetric CO_2 stretching bands, respectively [9]. The film dried at 310 °C shows a relatively large asymmetric CO_2 stretching band at about 1530 cm^{-1} and the other symmetric CO_2 stretching bands at 1340, 1400, and 1440 cm^{-1}. Fig. 4 clearly shows that the intensity of the asymmetric CO_2 stretching band appears to decrease as the drying temperature increases. In contrast with the asymmetric CO_2 stretching band, the symmetric CO_2 stretching band shows a smaller decrement with the drying temperature. We will speculate in this study that the organic residue showing an asymmetric CO_2 stretching band affects the nucleation and growth of the perovskite grains and is a possible cause of the preferred orientation.

There are two possible effects of the organic residue on the crystallization of the perovskite grains. The organic residue may serve as a heterogeneous site depending on the surface energy of the residue. The

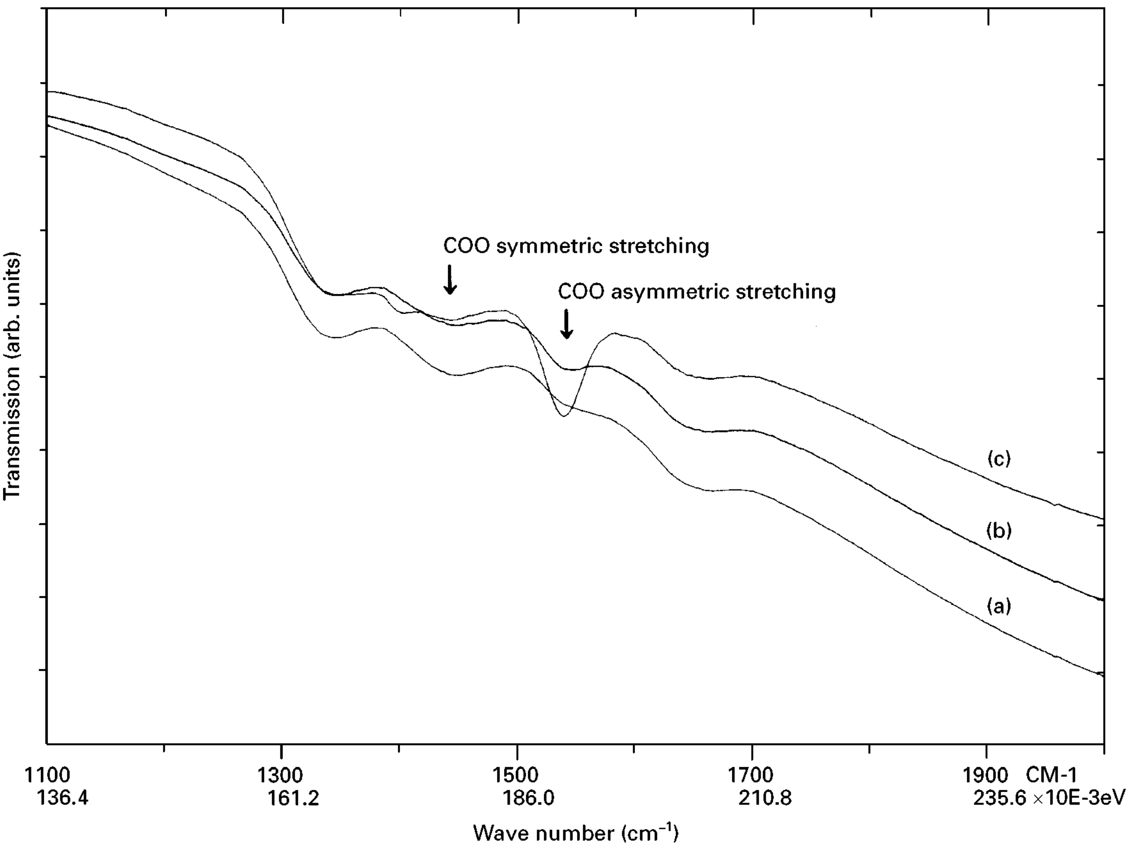

Figure 4 FTIR spectra of PZT films deposited on Pt/Ti/glass substrates and dried at (a) 310 °C, (b) 330 °C and (c) 350 °C for pyrolysis.

organic residue may also affect the growth rate of the perovskite grain. Both effects may affect the nucleation or the growth of the perovskite grains and, consequently, the preferred orientation of the film. We speculate that the observed (1 1 1) preferred orientation for the films dried at 310 and 330 °C may be due to nucleation being started mostly at the interface between the film and the electrode ((1 1 1) oriented Pt). Because the organic residue was present in the film, the growth rate may be relatively low, and the grains grew with (1 1 1) preferred orientation. Relatively weak (1 0 0) and (1 1 0) peaks were also observed in the film dried at 310 °C, which may be due to a relatively large amount of the organic residue affecting the nucleation of the perovskite phase as heterogeneous nucleation sites. Nucleation and growth may be started from the bulk and the surface as well as the interface of the film; grains having orientations than (1 1 1) also grew, and the film showed other orientations than (1 1 1). As the organic residue decreased as drying temperature increased to 350 °C, the growth rate increased, and the orientation of the film was changed to (1 0 0) preferred orientation due to the self-textured F-face growth of the lowest surface energy.

To test the above speculation, the films were fabricated with different thicknesses but dried and heat treated at the same temperatures, and the observations made in the orientations of the films will be compared with the above speculation. Fig. 5 shows the XRD patterns obtained for the PZT films fabricated with different coating cycles. All films were dried at the same temperature of 330 °C for 5 min after coating at each cycle. It is expected that the relatively thin films showed (1 0 0) orientation because it contained less organic residue but the thick films showed (1 1 1) orientation due to the relatively large amount of organic residue. All films were finally heat treated at 650 °C using RTA for 1 min. The patterns show that the grain orientation of the film strongly depends on the coating cycle. All films consist of the perovskite

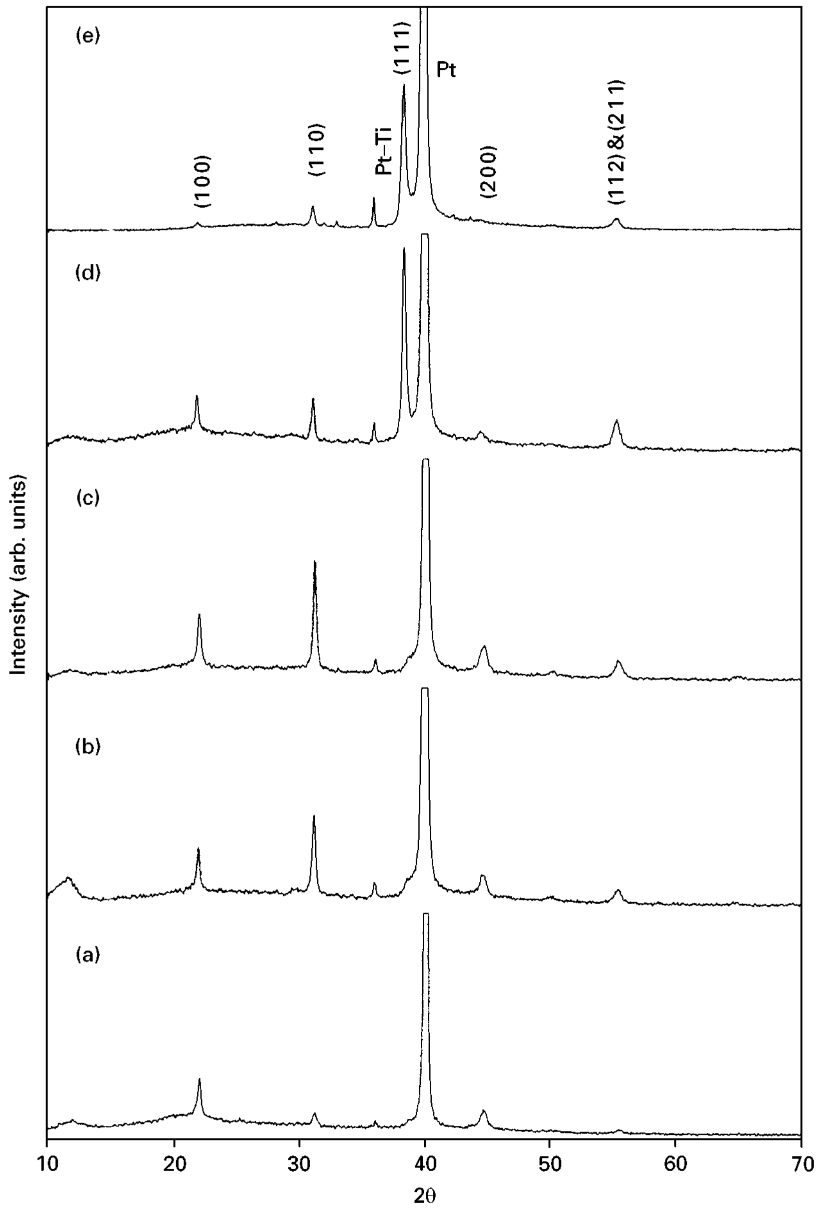

Figure 5 The X-ray diffraction patterns of the PZT films fabricated with different coating cycles: (a) 3, (b) 5, (c) 7, (d) 9 and (e) 11 cycles. The films were dried at 330 °C and heat treated at 650 °C using RTA for 1 min.

phase without any detectable pyrochlore phase. The Pt–Ti intermetallic compound peak was weakly observed as indicated on the XRD patterns. The films coated up to 7 cycles show both (1 0 0) and (1 1 0) peaks. The (1 1 0) peak was not expected in the above prediction. The relative intensity of the (1 1 0) peak increased as the coating cycle increased. The (1 1 1) peak was not detected in the XRD patterns of the films as expected in the above prediction. The intensity of the (1 1 1) peak, however, suddenly increases as the coating cycle increased from 9 coating cycles. The observations made in the coating cycle experiment are fairly consistent with the speculation given in the prior section. Fig. 6 shows FTIR spectra of PZT films fabricated with different coating cycles and dried at the same temperature of 330 °C. The films fabricated with up to 7 coating cycles did not show CO_2 symmetric and asymmetric stretching bands between 1400 and 1600 cm^{-1}. For the film fabricated with 9 coating cycles, however, showed the CO_2 symmetric and asymmetric stretching bands between 1400 and 1600 cm^{-1}. These observations may indicate that the presence of the organic reside may contribute to the formation of the (1 1 1) preferred orientation.

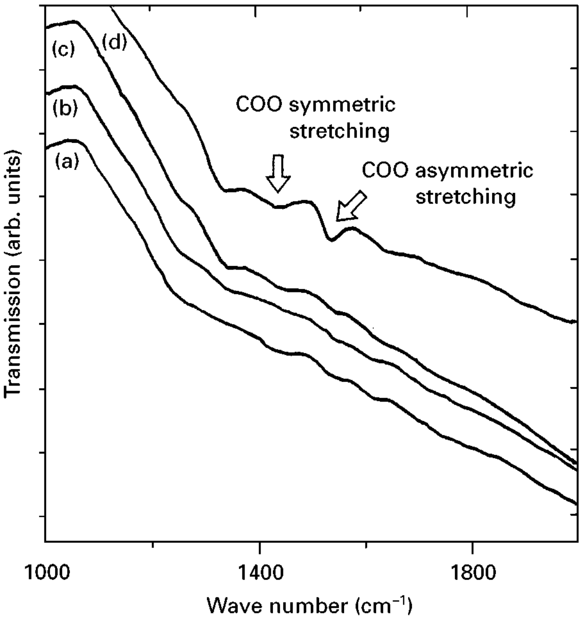

Figure 6 FTIR spectra of PZT films fabricated with different coating cycles: (a) 3, (b) 5, (c) 7 and (d) 9 cycles. The films were dried at 330 °C and heat treated at 650 °C using RTA for 1 min.

It was expected that the films dried at 350°C show (1 0 0) orientation independently of the coating cycle because the organic residue was already lowered by the drying temperature. Fig. 7 shows the XRD patterns of the PZT films fabricated with different coating cycles but dried and heat treated at the same temperatures of 350 °C and 650 °C, respectively. All films show (1 0 0) preferred orientation independent of the coating cycle, as expected. As the coating cycle increased, the relative intensity of the (1 0 0) peak increased, which may be due to film thickness. However, the orientation of PZT thin films dried at 350 °C did not depend on the coating cycles. This may be attributed to the relatively low content of the organic residue in the film dried at 350 °C as observed in the FTIR spectra (Fig. 4).

In order to confirm the above speculation in which the organic residue affects the formation of the film orientation, we conducted a study for the preferred orientation formation of the films dried for different drying times. It was expected that longer drying may decrease the organic residue and change the film orientation from (1 1 1) to (1 0 0). Fig. 8 shows the XRD

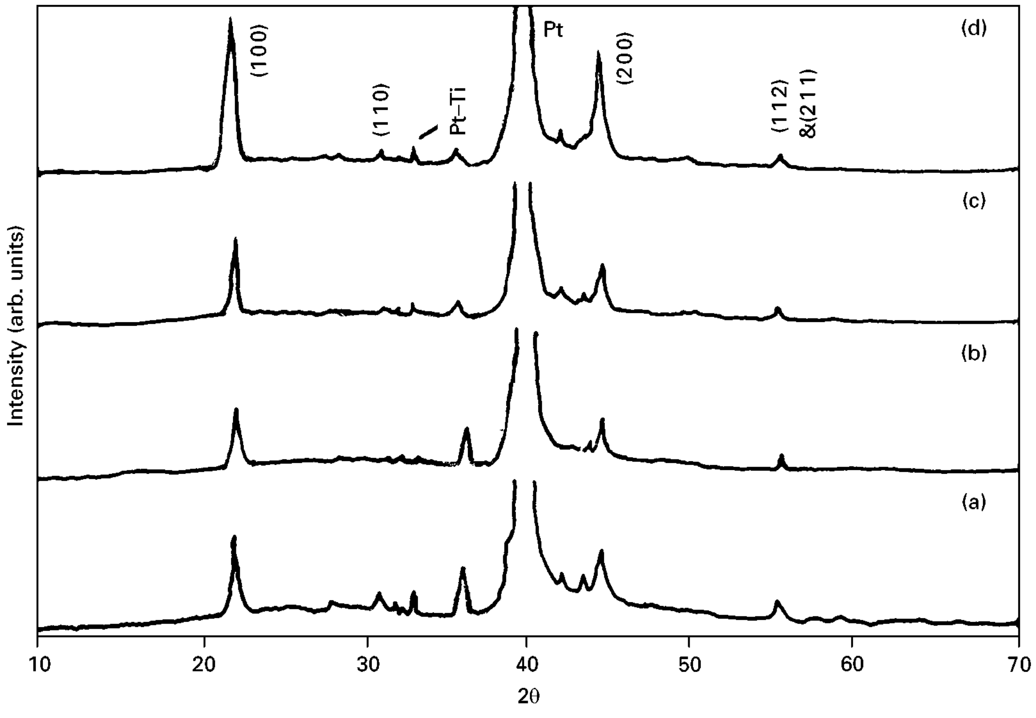

Figure 7 The X-ray diffraction patterns of the PZT films fabricated with different coating cycles: (a) 3, (b) 5, (c) 7 and (d) 9 cycles. The films were dried at 350 °C and heat treated at 650 °C using RTA for 1 min.

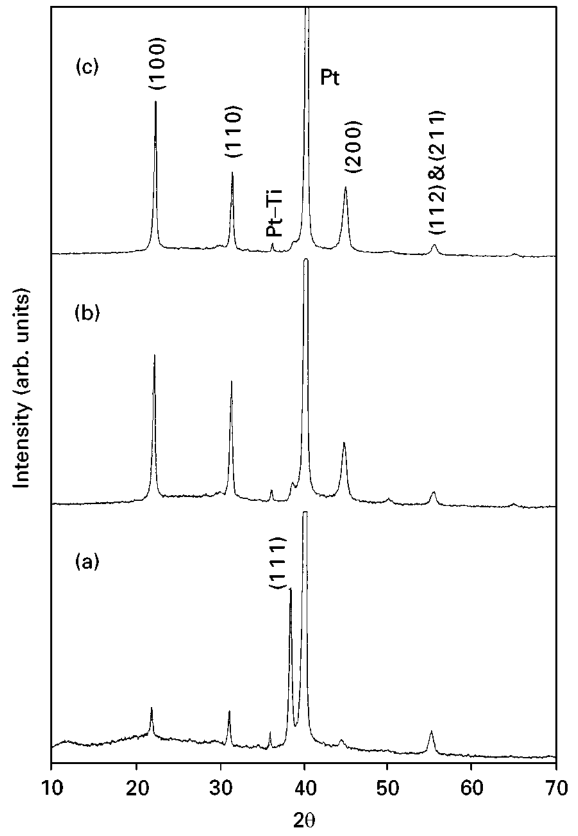

Figure 8 The X-ray diffraction patterns of the PZT films dried at 330 °C for different drying times: (a) 5, (b) 30 and (c) 60 min. The films were heat treated at 650 °C using RTA for 1 min.

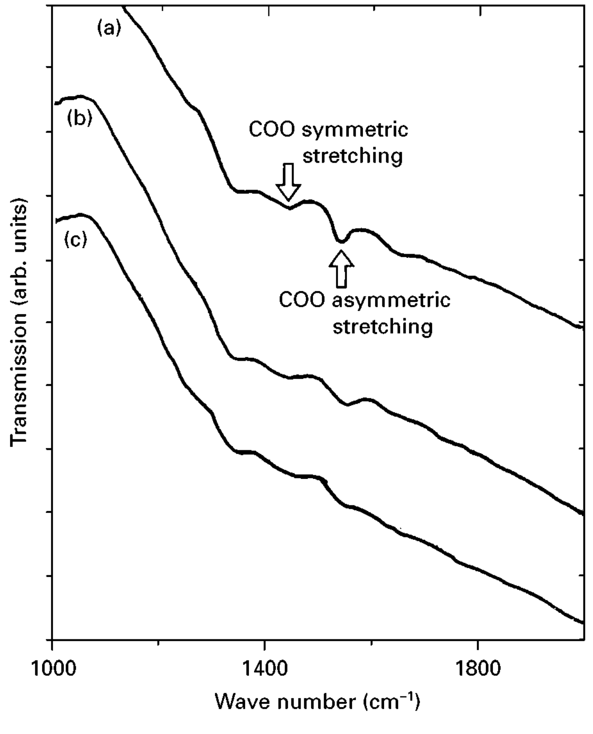

Figure 9 FTIR spectra of PZT films dried at 330 °C for different drying times: (a) 5, (b) 30 and (c) 60 min. The films were heat treated at 650 °C using RTA for 1 min.

patterns of the PZT films fabricated with 9 coating cycles and dried at 330 °C for different times but heat treated at the same temperature of 650 °C using RTA for 1 h. The film dried for 5 min shows (1 1 1) preferred orientation. As the time increased, however, the intensity of the (1 0 0) peak increased significantly while that of the (1 1 1) peak decreased significantly as expected. Fig. 9 shows FTIR spectra of PZT films dried for different drying times. In the case of the film dried for 5 min, the asymmetric CO_2 stretching band was observed between 1550 and 1600 cm^{-1}. In the films dried for 30 and 60 min, however, the asymmetric CO_2 stretching band as well as symmetric CO_2 stretching band was hardly detected. The films dried for 30 and 60 min also showed the (1 1 0) peak. A possible cause of the formation of the (1 1 0) orientation was not clear in this study, but the presence of the pylochore phase after the film dried (which was detected in the XRD pattern) and/or the possible nucleation at the surface and the bulk may affect the orientation of the film. The former is less likely because the relative intensity decreased as the film was dried for longer. The drying time was also varied for the films dried at 350 °C, and it was found that the (1 0 0) preferred orientation was not changed as expected based on the speculation. The films dried for 30 and 60 min also showed (1 1 0) orientation, and the relative intensity decreased as the film was dried for longer.

4. Conclusions

We have studied a possible cause of the different preferred orientation formation of sol–gel derived PZT thin films with different drying temperatures for pyrolysis. We have fabricated (1 0 0), (1 1 1) and mixed oriented PZT thin films on Pt/Ti/glass substrates by controlling the drying temperature in a sol–gel method. It was speculated that the amount of organic residue affects the nucleation and the growth and, consequently, the formation of the film orientation. Because the organic residue was present in the film dried at relatively low temperature, the growth rate may be relatively low, and the grains grew with (1 1 1) preferred orientation due to the (1 1 1) oriented Pt bottom electrode. As organic residue decreased as drying temperature increased, the growth rate increased, and the orientation of the film was changed to (1 0 0) preferred orientation due to the self-textured F-face growth of the lowest surface energy. The above speculation was tested using drying temperature, coating thickness (or cycle) and drying time. The films dried at 310 and 330 °C for 5 min had a relatively large amount of organic residue and showed (1 1 1) preferred orientation after annealing at 650 °C. The films showed symmetric and asymmetric CO_2 stretching bands in their FTIR spectra, whereas the film dried at 350 °C had no such bands and showed (1 0 0) preferred orientation. The orientation of the film dried at 330 °C was changed from mixed (1 0 0) and (1 1 0) orientation to (1 1 1) as the coating cycle increased as expected based on the speculation. On the other hand, for the film dried at 350 °C, the bands were not detected by FTIR, and the (1 0 0) orientation of the film was not changed with coating cycle. As the drying time increased for the films dried at 330 °C, the orientation of the film was changed from (1 1 1) to (1 0 0) as expected based on the speculation.

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References

1. C. T. LIN, .B W. SCANLAN, J. D. MCNEILL, J. S. WEBB and L. LI, *J. Mater. Res.* **7** (1992) 2546.
2. S. YOKOYAMA, Y. ITO, K. ISHIHARA, K. HAMADA, S. OHNISHI, J. KUDO and K. SAKIYAMA, *Jpn. J. Appl. Phys.* **34** (1995) 767.
3. N. NEUMANN, R. KÖHLER and G. HOFMANN, *Integrated Ferroelectrics* **6** (1995) 213.
4. D. L. POLLA and P. J. SCHILLER, *ibid.* **7** (1995) 359.
5. C. J. KIM, D. S. YOON, J. S. LEE, C. G. CHOI, W. J. LEE and KWANGSOO NO, *J. Appl. Phys.* **76** (1995) 7478.
6. C. J. KIM, D. S. YOON, J. S. LEE, C. G. CHOI and KWANGSOO NO, *Jpn. J. Appl. Phys.* **33** (1994) 2675.
7. T. TANI, Z. XU and D. A. PAYNE, in "Ferroelectric Thin Film III", edited by E. R. Mayers, B. A. Tuttle, S. B. Desu and P. K. Lansen (MRS, Pittsburgh, PA, 1993) p. 269.
8. C. D. E. LAKEMAN, J. F. CAMPION and D. A. PAYNE, in "Ceramic Transactions", Vol. 25, edited by A. S. Bhalla and K. M. Nair (The American Ceramic Society, Westerville, Ohio, 1992) p. 413.
9. N. B. COLTHAP, *J. Opt. Soc. Amer.* **40** (1950) 397.

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