

Properties of Lead Zirconate Titanate Thin Films Prepared Using a Triol Sol–Gel Route

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Microstructure and phase development during the thermal of precursor decomposition sol-gel coatings of $PbZr_{0.53}Ti_{0.47}O_3$ on platinized silicon substrates have been investigated for a triol sol-gel route. The single-layer, 0.4 µm PZT films were heated from below the substrate, over the temperature range 350-600°C, using a calibrated hot plate. The first crystalline phase to appear was a PbPt₃ intermetallic phase at the Pt/PZT interface. Although perovskite PZT formed at ca. 500°C, heating at higher temperatures, for example 550°C for 30 min, was required to develop ferroelectric hysteresis loops. However, the rather low value of remanent polarization, $P_r = 11 \ \mu C \cdot cm^{-2}$, was consistent with incomplete crystallization at 550°C. The values of remanent polarization increased with increasing processing temperatures, reaching 21 μ C·cm⁻² for samples heated at 600°C, with a corresponding E_c value of 57 kV·cm⁻¹. Distinctive spherical precipitates up to ca. 50 nm in size have been identified by TEM in the lower portions of otherwise amorphous coatings, after heating at around 350-400°C. Although their precise composition could not be identified, they were mostly Pb-rich, and it is speculated that they form due to reduction of some of the lead(II) acetate starting reagent, to atomic Pb during the early stages of thermal decomposition of the organic components of the gel; it is possible that subsequent reactions occur to form lead oxides or carbonates. High levels of porosity were present in many of the fully crystallized films. The possible reasons for this are discussed.

I. Introduction

Lead ZIRCONATE TITANATE (PZT) thin films have potential applications in various microelectronic systems, including capacitors, ferroelectric memory devices, piezoelectric micro-actuators, and pyroelectric thermal sensors. For a number of years we have been studying sol-gel routes based on 1,3-propanediol solutions of lead acetate, zirconium propoxide, titanium propoxide, and 2,4-pentanedione (acetylacetone). The diol-based sol-gel route^{1,2} offers the advantage of preparing thicker films than other, more established sol-gel routes.^{3,4}

Another sol-gel route, based on the triol 1,1,1tris(hydroxymethyl)ethane, $CH_3C(CH_2OH)_3$, has recently been developed in this laboratory.^{5,6} The new 1,1,1tris(hydroxymethyl)ethane, or "triol" route produces crack-free, single-layer films up to ca. 1 µm in thickness, which is a value similar to that of the diol route. However, the incidence of other macrodefects, such as surface pores, increases with thickness, imposing an upper limit of ca. 0.5 µm for producing high-quality, mirror-like surfaces. Because of faster rates of gelation, the triol sols exhibit more favorable coating characteristics than diol precursors, and we have found it easier to fabricate high-quality films using the triol process.

A feature of sol-gel derived PZT films is a characteristic preferred orientation observed in X-ray diffraction patterns. Often this is imparted by the underlying substrate/electrode configuration; in the present work the substrate was Pt/Ti/SiO₂/Si, in which the polycrystalline platinum electrode had crystallized with a (111) orientation in the plane of the substrate. During thermal processing of the coated substrate, some of the original lead acetate in the sol-gel coating is reduced to atomic lead at low temperatures, and this then reacts with the Pt layer to form a PbPt₃ intermetallic phase, also displaying (111) orientation,⁷⁻¹⁰ before being oxidized at higher temperatures. Because of lattice matching between PZT and Pt, and more specifically PbPt₃,¹¹ there is a tendency for PZT nucleation to proceed initially by heterogeneous nucleation at the electrode interface. Because of the (111) orientation of the Ptbased bottom electrode, the coatings preferentially nucleate with a (111) orientation at the bottom interface, since the energy barrier for (111) oriented nuclei is lowered by lattice matching. Other orientations later nucleate within the bulk of the film. The relative extent of interfacial oriented nucleation and growth, in comparison with nucleation in the bulk of the film, is dependent on process conditions.

Some workers have reported that a $PtTi_x$ interface layer can form, which also influences PZT film orientation.¹² Furthermore, under certain conditions it is also possible to produce strongly (100) oriented PZT films, which may indicate that crystallization has occurred in the absence of the PbPt₃ interfacial layer.

In the present work we report on phase development, microstructure, and ferroelectric properties for thin films produced by heating triol gel coatings on platinized silicon substrates using a simple form of rapid thermal annealing in which all heating steps are performed using a calibrated hot plate. Usually, after a first heat treatment on a hot plate at $300-400^{\circ}$ C, the sample would be transferred to a furnace, or a rapid thermal annealing unit, to complete the crystallization process. Potentially, performing all thermal treatments on the one hot plate is a convenient means of processing sol–gel thin films, but may produce differences in film properties.

II. Experimental Procedure

Sols were prepared from lead acetate $[Pb(OOCCH_3)_2(H_2O)_3,$ Alfa, 99+%], titanium(IV) diisopropoxide bispentanedionate $[Ti(O^{iso}Pr)_2(CH_3COCHCOCH_3)_2,$ Alfa, abbreviated TIAA, 75 wt% in isopropyl alcohol], zirconium(IV) *n*-propoxide $[Zr(O^nPr)_4,$ Aldrich, 70 wt% in 1-propanol], 2,4-pentanedione [acetylacetone, CH₃COCH₂COCH₃, abbreviated acacH, Aldrich, 99+%], and 1,1,1-tris(hydroxymethyl)ethane [CH₃C(CH₂OH)₃, Aldrich, 99%].

First, 2.976 g of zirconium *n*-propoxide was mixed with 1.286 g of acetylacetone under a dry nitrogen atmosphere. The solution was heated at ca. 90°C for 2 h. After cooling, 2.739 g of titanium diisopropoxide bisacetylacetonate, 5.234 g of lead acetrate trihydrate, and 2.912 g of 1,1,1-tris(hydroxymethyl)ethane were added to the solution. The solution was then heated at \sim 70°C for 4 h. At

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the final stage the solution concentration was $1.21 \text{ mol}\cdot\text{dm}^{-3}$. Then for spin coating purposes the sol was diluted to 0.75 mol·dm⁻³ with 2-methoxyethanol; sols contained 10 mol% excess lead acetate.

Sols were deposited on Pt/Ti/SiO2/Si substrates (supplied by GEC-Marconi Technology); the Pt layer was 1000 Å thick, the Ti adhesion layer 50 Å, and the thermally grown SiO₂ 3600 Å. The Pt bottom electrode was polycrystalline with a (111) orientation. The substrates used for film deposition were cut into $\sim 1 \text{ cm}^2$ pieces, and cleaned ultrasonically with a series of cleaning solvents: Analar grade trichloroethylene, Analar grade acetone, and finally, 2-propanol for 3 min each. The substrates were dried at $\sim 100^{\circ}$ C before coating.

For sol deposition, the sols were syringed though an in-line 0.2 µm Nylon membrane filter (Pall Trinity Micro Corp., NY); all of the substrate was covered with the sol before spin coating at a speed of 3000 rpm, for 1 min. The coated substrates were then routinely heat-treated at 400°C for 10 min on a custom-built hot plate consisting of a stainless-steel cylindrical block (diameter = 16 mm, length = 30 mm) which was heated using internal electrical heating elements. The block temperature was measured by using a K-type thermocouple inserted into the steel block, and by a contact thermocouple pressed onto the surface of the block (Model PI8008 supplied by BDH Chemicals, U.K.); hereafter, these are referred to as the "block thermocouple" and the "surface contact thermocouple," respectively. In order to avoid variations in temperature caused by the effects of variable air flows over the sample, the hot plate (which was located in a fume cupboard) was shielded using a cylindrical collar, 15 cm high and 20 cm in diameter.

After the films were annealed at 400°C for 10 min, they were removed from the hot plate and, after the temperature was raised, replaced for a further heat treatment of 30 min duration at various temperatures-450°, 480°, 500°, 520°, 550°, 565°, 580°, or 600°C. Over a 30 min period, the temperature of the block was found to fluctuate by only $\pm 3^{\circ}$ C.

Phase development was monitored using X-ray diffraction (Phillips APD 1700 using CuK α radiation); XRD peak intensities are quoted in terms of peak heights. Scanning electron microscopy (Hitachi S700 field emission SEM) was used to examine microstructural features and a Radiant Technologies (RT66a) ferroelectric tester was used to measure the polarization-electric field (*P*–*E*) response at 60 Hz for a 300 kV·cm⁻¹ wave form. Gold dot electrodes, 0.3 mm in diameter, were sputtered onto the film using shadow masking; a corner of the PZT film was etched to reveal the bottom Pt electrode. For each sample, 10 dot capacitors were tested; average values are reported for remanent polarization, $P_{\rm r}$, where $P_r = (|+P_r| + |-P_r|)/2$, and coercive field, $E_c = (|+E_c| + E_c)$ $|-E_{c}|)/2.$

TEM samples were prepared in cross section via the conventional "sandwich" method.¹⁸ The disks were dimpled to ca. 50 µm thickness and subsequently thinned to electron transparency using a Gatan PIPS low-angle, low-accelerating-voltage ion beam thinner. These were examined in a Philips CM20 TEM/STEM operating at 200 keV, and fitted with a SATW thin window EDX detector (Oxford Instruments) and PEELS spectrometer (Gatan). Further investigations were performed using a Philips CM200 field emission TEM equipped with a Gatan imaging filter, for energy filtered imaging (EFTEM)

III. Results

A commercial specialist wafer thermocouple was not available to us; instead two conventional thermocouple configurations were used to monitor the temperature experienced by the films during thermal decomposition. Before commencing the film decomposition experiments, the accuracy of each thermocouple reading was assessed. The temperature readings from the thermocouple inserted into the block were consistently higher by around 10% than the equivalent readings from the surface thermocouple. The lower reading from the surface contact thermocouple reflects problems in

making good physical contact between the surface of the block and the thermocouple.

The accuracy of each thermocouple in monitoring the temperature that would be experienced by a sol-gel coating was investigated by smearing finely ground powders of two compounds, potassium iodate (mp 560°C) and 1,1,1-tris(hydroxymethyl)ethane (mp 200°C) onto a Pt/Ti/SiO₂/Si substrate. The temperature of the hot plate was then increased slowly from room temperature using a heating rate of 2° C·min⁻¹; the experimentally observed melting temperatures, as measured by the two thermocouples, are compared against the known melting temperatures¹³ in Table I.

There was a close similarity between known and experimentally determined melting temperatures measured from the block thermocouple. This confirmed that thermal equilibrium between the heated block and the silicon wafer was established, and that the block thermocouple readings would be a reliable indicator of the temperatures experienced by the PZT gel precursor coatings during hot-plate thermal processing steps. Hot-plate temperatures quoted in the remaining text therefore refer to the block thermocouple readings.

The effective heating rate experienced by the sol-gel coatings was assessed by preheating the hot plate to 600°C and observing the time period for potassium iodate powders to melt; this corresponded to a heating rate of $\sim 100^{\circ} \text{C} \cdot \text{s}^{-1}$.

X-ray diffraction patterns, after heating the coated substrates at 400°C for 10 min, and then for 30 min at either 400°, 500°, or 550°C, again on the hot plate, are shown in Fig. 1. After heating at 400°C, there was a sharp and intense XRD peak at 38.6° 20, together with a faint, broad hump centered at $29.1^{\circ} 2\theta$ (Fig. 1(a)). The sharp peak at a *d*-spacing of 2.33 Å is attributed to the PbPt₃ transitory interfacial phase which forms in the reducing atmosphere existing at the substrate-film interface during the decomposition of organic components at low temperatures.⁸⁻¹⁰

The very broad peak at 29.1° 20 is a common feature in sol-gel PZT films, and is usually attributed to poorly crystallized or fine-grained intermediate phase(s) having a pyrochlore or flourite crystal structure.14,15

The first faint perovskite PZT peaks appeared after heating a sample at 480°C, but the broad peak around 29.1° 2θ continued to be present and there was still evidence of the PbPt₃ phase. When the temperature was increased to 500°C, a slight shift in d-spacing from 2.33 Å for the 400°C sample to 2.35 Å for the 500°C sample (and also for samples heated at higher temperatures) occurred, and the peak profile became less sharp (Fig. 1(b)). This slight increase in *d*-spacing, of what was assigned to be a 111 peak of PbPt₃ in the 400°C sample, is consistent with the peak at higher process temperatures being now principally due to 111 PZT,¹¹ rather than PbPt₃.

The variation in the intensity of the 111 PZT peak was expressed in terms of a parameter α_{111} , where $\alpha_{111} = I_{111}/(I_{100} +$ $I_{110} + I_{111}$; the increase in (111) preferred orientation over the temperature range 520° to 600°C is displayed graphically in Fig. 2. The increasing relative intensity of the 111 PZT peak above 500°C indicates the development of a progressively greater proportion of (111) oriented PZT crystallites in films which were processed at higher temperatures. Other perovskite X-ray peaks also became sharper and more intense in samples heated at 550° or 600°C, indicating improved crystallization throughout the film (Fig. 1(c)).

Cross-sectional TEM studies provided more detailed information on phase development. Initially, samples heated at low

Table I. Thermocouple Calibration against Known Melting Points of 1,1,1-Tris(hydroxymethyl)ethane (THOME) and **Potassium Iodate**

Substance	mp (°C)	Thermocouple calibration (°C)	
		Inserted thermocouple	Surface thermocouple
THOME KIO ₃	200 560	203 564	183 510



Fig. 1. X-ray diffraction plots for films heated at 400° C for 10 min followed by heating for 30 min at (a) 400° , (b) 500, and (c) 550°C.

temperatures were examined, confirming the formation of a crystalline intermetallic phase at the bottom Pt electrode. For example, Fig. 3(a) shows the bottom interfacial region of a sample heated at 400°C for 30 min, indicating the interfacial layer to be crystalline (Fig. 3(b)), with a depth of ~25 nm. A similar thickness was observed for a sample heat-treated at 350°C. From spot analysis by STEM/EDX, the composition of the layer was found to be PbPt₃, which is in agreement with previous studies.⁹ There were local variations in the thickness of this layer, including regions, particularly at columnar grain boundaries in the Pt electrode, where short circuit diffusion pathways for Pt gave rise to convex hemispherical irregularities, as shown to the left of the arrow in Fig. 3(a).

Because the interfacial phase becomes unstable in oxidizing conditions,¹⁰ the amount of PbPt₃ is a function of process temperature and time.⁸ Consequently the average thickness of the PbPt₃ layer in our films decreased for process temperatures above 400°C. A very thin interfacial layer was still evident in the sample heated at 600°C (Fig. 4); however, because the layer was now only around 5 nm in thickness, it was not possible to confirm its composition. No discrete interface layer was observed in a film heat-treated at 700°C.

It was apparent from both bright-field diffraction and phase contrast lattice imaging of samples heated at 500°C or higher that immediately above the bottom electrode, columnar grains of the perovskite phase were closely aligned with the (111) orientation of



Fig. 2. Variation in intensity of the 111 PZT peak expressed in terms of a parameter α_{111} , where $\alpha_{111} = I_{111}/(I_{100} + I_{110} + I_{111})$.

the underlying electrode, as shown for a film heat-treated at 600° C in Fig. 5.

Grain sizes in the films annealed between 500° and 600° C showed an increase from ca. 0.2 to 0.3 μ m, with many columnar grains growing through the full film thickness. A few pockets of nanosize grains were present, attributed to a pyrochlore intermediate phase, as indicated in XRD plots.^{14,15} Most of these pockets were concentrated near the surface of the film.

While the above structural information is fairly typical of sol-gel PZT films, we have observed unexpected microstructural features in films heated at low temperatures, for which there is little published information. Spherical particles, up to ca. 50 nm in diameter, consistently appeared in samples heated at low temperatures, for example 350°C for 30 min. These were located in the lower portions of the otherwise amorphous ca. 0.4 µm thick films (Fig. 6). Some pores of similar morphology to the particles were also present; these may have formed due to elimination of some of the precipitates during TEM sample preparation. At higher magnifications, and from SAED patterns, the precipitates were shown to be polycrystalline, exhibiting lattice spacings of around 0.3 nm (Fig. 7). There was also evidence of discrete single crystallites (Fig. 7(a)); presumably single crystallites coalesced to form the larger, approximately spherical polycrystallites. Athough it was difficult to obtain accurate information on chemical and physical structure because of the small particle dimensions, scanning TEM and EFTEM indicated that many of the spherical polycrystalline particles were lead-rich. Other authors have reported precipitates similar in form to those described above; they suggested that the precipitates were PbO,¹⁶ thought to arise directly from excess lead acetate added to the starting sols.

Fully crystallized films exhibited high levels of porosity, with pore sizes ranging up to ca. 50 nm. A porous region of a film heated at 600°C, showing both inter- and intragranular pores, is highlighted in Fig. 8. Possible causes of this porosity are discussed below.

For samples heated on the hot plate at 520°C for 30 min, the polarization–electric field (*P–E*) loop was a broad ellipse, consistent with a lossy dielectric.¹⁷ The XRD patterns and TEM had indicated the presence of perovskite PZT at \geq 500°C, together with the pyrochlore phase; therefore the nonferroelectric *P–E* response of the 520°C sample probably reflects the dominant influence of intermediate nonferroelectric phase(s), and any amorphous material in the film. The small grain size of the perovskite phase at these low temperatures could also suppress domain switching and prevent *P–E* hysteresis.



(a)



Fig. 3. (a) TEM bright-field image of a PZT film after heating on a hot plate at 400° C for 30 min; (b) corresponding selected area electron diffraction pattern from the interfacial layer.



Fig. 4. TEM bright-field image of a PZT film after heating on a hot plate at 400°C for 10 min followed by a treatment at 600°C for 30 min; the arrow highlights a narrow 5 nm interfacial layer.



Fig. 5. TEM bright-field image of a PZT film after heating on a hot plate at 400°C for 10 min followed by a treatment at 600°C for 30 min showing $\langle 111 \rangle$ lattice fringes near the bottom electrode.

Heating a film at 550°C for 30 min resulted in the onset of ferroelectricity (Fig. 9(a)), with $P_r = 11 \ \mu \text{C} \cdot \text{cm}^{-2}$, and $E_c = 66 \text{ kV cm}^{-1}$. Increasing the temperature to 600°C produced an increase in measured polarization values, P_r reaching 21 $\mu \text{C} \cdot \text{cm}^{-2}$ for the 600°C sample (Fig. 9(b)). This was accompanied by a slight decrease in coercive field, from 66 to ca. 55 kV·cm⁻¹. The reduction in coercive field may in part be due to an increase in grain size; TEM data showed that the estimated average grain size increased from around 0.2 μm in the 550°C sample to 0.3 μm in the 600°C sample. Progressive changes in values of remanent polarization and coercive field are plotted in Fig. 10.

IV. Discussion

The combined results of XRD and TEM are indicative of the extended growth of a (111) preferentially oriented PZT layer which originates during the earliest stages of crystallization from the bottom electrode. As stated in the Introduction, there is a close lattice match between Pt and PZT(53/47), but the match between PZT and the PbPt₃ interfacial layer, identified here by TEM, is closer, with a difference in d_{111} spacing of ~1% as opposed to ~4% for Pt;¹¹ there are also structural similarities between the



Fig. 6. TEM micrograph of a sample heated at 350°C for 30 min, showing spherical particles in an amorphous matrix; pores are indicated by arrows.



(a)



Fig. 7. (a) TEM micrograph of a sample heated at 350°C for 30 min. (b) Selected area electron diffraction pattern obtained from the polycrystalline particle.

(111) atom/anion arrangements in each structure. Hence the (111) oriented PbPt₃ layer is considered to be the principal reason for (111) PZT film preferred orientation. The interface layer lowers the nucleation energy of (111) oriented PZT crystallites which therefore grow preferentially from the bottom electrode. This, together with subsequent nonoriented nucleation within the bulk of the film, gives an overall (111) preferred orientation in XRD patterns.

In comparison to films made previously by the same triol sol-gel processing route, but for which the final heat treatment took place in a tube furnace, the present hot-plate samples exhibited a greater level of (111) orientation. For example, samples heated at 600°C in a tube furnace^{18,19} showed an orientation parameter $\alpha_{111} = 0.5$, compared with $\alpha_{111} = 0.8$ for the hot-plate samples. Although the time scales over which a temperature gradient exists across the film must be very short, the



Fig. 8. TEM micrograph of a sample heated at 400°C for 10 min and 600°C for 30 min showing (a) intergranular and (b) intragranular porosity.

higher (111) preferred orientation in films heated from below the substrate could suggest that this pseudo unidirectional heating drives the formation and growth of crystallites off the bottom electrode more effectively than for samples heated uniformly in a tube furnace. In furnace samples, a greater proportion of crystallization in the film would occur from nucleation in the bulk, or at the top surface of the film which is not subject to the orientating influence of the bottom interface, thereby reducing measured (111) orientation.

However, as well as differences in the direction from which the coatings were heated, the rates of heating were also different. Heating rates were faster on the hot plate, $\sim 100^{\circ} \text{C} \cdot \text{s}^{-1}$, compared with $2^{\circ} \text{C} \cdot \text{s}^{-1}$ for furnace firing. Hence different stress levels may exist during crystallization which could also affect the extent of preferred orientation.

Differences were also obseved in the *P*–*E* response. The hysteresis loops of the hot-plate samples were broader than those of corresponding furnace samples; hence the E_c values for hot-plate samples were significantly higher, e.g., 57 kV·cm⁻¹ compared with 40 kV·cm⁻¹ for furnace samples heated at 600°C.^{18,19} The broader *P*–*E* loops, and higher E_c values, may be due to greater residual stresses in the more rapidly unidirectionally heated hot-plate samples, but the grain size was also smaller in hot-plate samples—both of which could restrict domain mobility and ferroelectric switching.

The high levels of porosity in the films, made either on the hot plate or in a furnce, is unsatisfactory for any proposed device applications. Clearly the further development of the triol sol-gel route requires that porosity be eliminated. It is noted that it is possible to prepare high-density 0.1 µm films by the triol route, and the films have a microstructure similar to 0.1 µm films prepared using an established acetic acid/methoxyethanol route¹⁸ (0.1 µm is the maximum crack-limiting single-layer thickness of established routes). The future challenge is to produce dense single films $>0.1 \ \mu m$ from the triol route. It is probable that porosity is linked to greater difficulties in eliminating organic decomposition vapors from the thicker single-layer sol-gel films. Hence more gradual low-temperature heating (instead of one step at 400°C) should be investigated in the future, to minimize structural disruption during organic decomposition, and thereby reduce porosity levels.

Cross-sectional TEM revealed approximately spherical particles or aggregates in triol-derived films. These were first observed in a



Fig. 9. Polarization–electric field hysteresis loops for PZT films heated at 400°C for 10 min followed by 30 min at (a) 550° and (b) 600°C.

sample annealed at 350°C for 30 min and were dispersed in an amorphous matrix; predominantly the precipitates were located in the lower portions of the film. The Pb-rich phase identified in many of the precipitates probably originates from chemical reduction of some of the (excess) lead(II) acetate starting reagent. The fact that they are not found near the surface of the films is consistent with a formation mechanism linked to chemical reduction. Diffusion distances for the escape of gaseous gel decomposition products increase as a function of film thickness; there will also be slower rates of inward diffusion of oxygen to the lower portions of the film. Hence the partial pressure of oxygen near the base of the 0.4 μ m films is presumably lower than in a 0.1 μ m film heated in the same manner. It is well known that reduction of Pb(II) to atomic Pb occurs at the bottom Pt interface in sol-gel PZT films, and that interdiffusion produces a layer of PbPt₃. However, in our thicker 0.4 µm single layers, lower partial pressures of oxygen at the base of the film could be promoting a greater incidence of Pb(II) reduction so that in addition to interfacial PbPt₃ there is a segregation and nucleation of atomic Pb within the film. These then coalesce to form the polycrystalline spherical particles in Fig. 7. A similar reduction reaction has been proposed to explain the presence of Pb and PbO, identified by XRD, in PZT powders formed by pyrolysis of various metalloorganic precursors after heating at 400-500°C,²¹ and we also have have obtained XRD evidence of Pb, formed by reduction of lead acetate, as an intermediate phase in the formation of PZT powders by spray pyrolysis of sol-gel precursor solutions.²²

Unfortunately because of the small dimensions of the particles, and the "contamination" of the EDX spectra by the surrounding



Fig. 10. Variation of P_r and E_c as a function of process temperature.

matrix, it was not possible to identify the structure and composition of this low-temperature phase. However, it is probable that even though the precipitates could originate from atomic Pb, oxidation and carbonation reactions could later produce lead oxides and carbonates. The origins and composition of these precipitates are under further investigation, as is their link to film porosity; the results of a detailed TEM investigation in conjunction with colleagues at the University of Sheffield will be reported in due course.²⁰ It is conceivable that as thermolysis proceeds, outward diffusion from the precipitates occurs, leaving residual pores that at least in part contribute to porosity in the final PZT films. Some Zr-rich precipitates have also been identified which could signify segregation of a Zr-rich PZT phase,¹⁸ but again the reasons for this are unclear.

V. Conclusions

Crystallization to perovskite PZT in the 0.4 μ m single-layer films started at around 500°C, but to obtain a ferroelectric *P*–*E* response, an annealing temperature of 550°C was required. However, improved ferroelectric properties were obtained in films heated at 600°C.

The P-E hysteresis loops were broader than for corresponding samples prepared in earlier studies using furnace annealing. The implication was that stress levels were higher in hot-plate samples due to the unidirectional nature of the heating process, and faster heating rates. Grain sizes and the levels of (111) preferred orientation also differed between the two heating methods which could have an impact on domain switching behavior.

At lower temperatures a PbPt₃ interfacial layer was identified in TEM film cross sections. The thickness of this layer was temperature-time dependent, which is consistent with previous studies. A coherent (111) oriented PZT layer was observed to grow outward from the (111) PbPt₃ layer, confirming the importance of the intermetallic phase on PZT preferred orientation.

Within the lower portion of the films, spherical precipitates, up to ca. 50 nm in diameter, were observed in TEM micrographs after treatment at 350°C. These were polycrystalline and mostly Pbrich, although Zr-rich regions were also identified by STEM/EDX. It is thought that these features could contribute to the high porosity in the fully decomposed PZT films. However, porosity may simply be caused by overly rapid heating rates during the expulsion of organic decomposition vapors, and therefore further research into the origins of porosity is required.

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