

Densification and enhanced polarisation in lead zirconate titanate sol–gel thin films

Anirban Chowdhury*, Mikael A. Khan, Craig James, Steven J. Milne

Institute for Materials Research, University of Leeds, Leeds LS2 9JT, UK

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ABSTRACT

Isopressing a $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ sol–gel coating prior to thermally induced crystallisation leads to increased remanent polarisation (P_r) values for optimum compaction pressures of ~ 125 MPa. The value of P_r increases from $25 \mu\text{C cm}^{-2}$ for a single layer $0.3 \mu\text{m}$ porous film prepared in the normal manner, to $34 \mu\text{C cm}^{-2}$ for an equivalent $0.2 \mu\text{m}$ dense film. Compaction pressures >135 MPa lead to little further increase in film density, but P_r decreases to values below those of non-pressed porous samples. The trends in polarisation are attributed to the balance between the beneficial effects of decreased porosity and the detrimental effects of increased strain levels in the films.

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1. Introduction

For several thin film ferroelectric device applications, such as piezoelectric MEMS, the film thickness should be of the micron scale. Solution deposition techniques developed in the mid 1980s are capable of producing high-quality lead zirconate titanate (PZT) films, but the thickness of a single layer is restricted to around $0.1 \mu\text{m}$. Thicker coatings crack due to process-induced strain. The original, and most commonly used, sol–gel PZT systems are based on methoxyethanol solutions of lead acetate, titanium propoxide and zirconium propoxide, with water additions to induce controlled hydrolysis and condensation reactions [1]. The sols are deposited onto metallised silicon or other substrates by spin-coating. Evaporation of solvent during spinning normally is sufficient to convert the liquid sol to a semi-rigid gel coating. Thermal conversion to PZT occurs in stages with the first heat treatments at 200 – 450°C to decompose organic components of the gel structure, followed by heating at 550 – 700°C to form a crystalline thin film product.

Several modifications to this base system have been demonstrated, some of which include acetic acid or acetylacetonate stabilising agents to simplify the sol-synthesis stage [2,3]. In order to produce micron-scale films, suitable for piezoelectric applications, many repeat deposition-heating cycles are required. As well as being time consuming, the increased thermal input may

promote deleterious interfacial reactions between film and substrate/electrode.

Several alternative sol–gel systems have been devised which offer an increase in single-layer film thickness, and hence may be useful in terms of fabricating multi-layer films in the 1 – $10 \mu\text{m}$ range using fewer deposition cycles. These include methods employing additions of a high-molecular weight polymer. Polyvinylpyrrolidone (PVP) was the first such example, giving a maximum single-layer thickness of $0.75 \mu\text{m}$ [4]. Subsequent variations of the heat treatment steps before final crystallisation produced single layers up to $2 \mu\text{m}$ in thickness on silica glass substrate [5]. High levels of porosity evident in SEM micrographs of these films presumably arise from structural disruption due to an increased quantity of vapours produced during the critical stages of thermal decomposition. Another approach uses additions of diethanolamine, but again significant porosity is evident in SEM sections of the resulting $0.7 \mu\text{m}$ single-layer films [6]. An earlier study used sols made from di- or tri-hydroxy alcohols (diols or triols) which actively participate in the sol–gel reaction, forming molecular bridges between metal centres [7,8]. Porosity has also been observed in some of these films [9].

By introducing a compaction step toward the end of the pyrolysis heating schedule, prior to film crystallisation, we demonstrated previously that the thickness of a PZT film from the diethanolamine route decreased from 0.7 to $0.2 \mu\text{m}$ [10]. However, cracks appeared in the resulting dense films. The decrease in thickness after compaction indicated that the thickness enhancement in the unpressed film arose because of a bloating effect associated with the escaping volatile organic species during the initial heat treatment stages. The absence of cracking in ‘thick’ films before compaction is a con-

* Corresponding author. Tel.: +44 113 343 2552; fax: +44 113 343 2384.

E-mail address: preac@leeds.ac.uk (A. Chowdhury).

sequence of a toughening mechanism afforded by the high-levels of porosity. Hence the dense PZT films from the diethanolamine route cracked after isopressing. Longitudinal cracks traversed the film section leading to electrical shorting when top electrodes were applied, and it was not possible to measure ferroelectric properties.

In the case of films made from a triol sol–gel route, we now demonstrate that the intermediate isopressing step can be applied to 0.3 μm single-layer PZT films without causing the films to crack after compaction. Therefore for the first time it has been possible to determine ferroelectric properties and to correlate electrical properties to processing conditions.

2. Experimental

Single-layer $\text{Pb}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3$ films were synthesised on platinised silicon substrates (Pikem, UK), using a triol-based sol–gel route [8]. Zirconium *n*-propoxide, 70 wt% in *n*-propanol [$\text{Zr}(\text{OC}_3\text{H}_7)_4$], titanium diisopropoxide bis dipentanedionate, 75 wt% in 2-propanol [$\text{Ti}(\text{OC}_3\text{H}_7)_2(\text{CH}_3\text{COCHCOCH}_3)_2$ abbreviated TIAA], lead (II) acetate trihydrate 99%+ and 1,1,1-tris(hydroxymethyl)ethane 99%, [$\text{CH}_2\text{C}(\text{CH}_2\text{OH})_3$ abbreviated THOME] were used to produce a $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ sol with 10 mol% of the Pb reagent in excess. Reagents were sourced from Sigma–Aldrich, UK. The sols, 0.75 M were deposited onto platinised silicon substrates, Pt(1 1 1)/Si(1 0 0). The substrates used for film deposition were cut using a diamond tip scribe into 10 mm \times 10 mm pieces, and cleaned ultrasonically with acetone and finally 2-propanol (15 min ultrasonic treatment for each solvent), followed by drying in a stream of nitrogen. The spin speed and time, along with organic burnout temperature and time, have been kept constant at 3000 rpm for 30 s, and 400 °C for 10 min, respectively, for all the films. The coatings were then isopressed at different pressures, 100, 125, 135, 150, 165 and 200 MPa, for 3 min (Stanstead Fluid Power, Stanstead, United Kingdom). The films were encapsulated in a double-layer latex sheath and evacuated for around 5 min using a vacuum pump, prior to compaction. This avoided air pockets and helped achieve a uniform applied pressure over the sample.

Compacted films were heat-treated at 700 °C for 30 min to convert the amorphous, isopressed film to crystalline PZT. X-ray diffraction was performed using an X-ray diffractometer (Philips APD 1700, Almelo, The Netherlands) with monochromatic Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). XRD pole figures were recorded about the (2 0 0) peak ($2\theta = 45.38^\circ$) using a PANalytical X'Pert PRO MPD with a texture stage: the angle ψ (Ψ) ranging from 0° to 90° with a step size of 2.5°, and the angle ϕ (Φ) ranged from 0° to 360° with a step size of 5°. The microstructure of the film in cross-section was observed using scanning electron microscopy, SEM, (LEO 1530 FEGSEM, and Cambridge, United Kingdom). Film thickness was obtained by observing SEM sections (estimated measurement error $\pm 30 \text{ nm}$). For electrical testing, the annealed films were sputter coated with gold dots, $\sim 300 \mu\text{m}$ in diameter, using a shadow mask method. The corners of the films were then etched away with hydrofluoroboric acid (HBF_4) until the platinum bottom electrodes were exposed. The polarisation–electric field (P – E) response was investigated using a RT66A ferroelectric tester (Radiant Technologies, Albuquerque, NM) at a frequency of 1 kHz. For each film, P – E data were recorded for 10 dot electrodes. Due to loop displacement along the field axis, values of E_c were calculated from: $E_c = [|-E_c| + |E_c|]/2$. Values of P_r were calculated in a similar manner.

3. Results and discussion

Films which had been fabricated in the normal manner (without pressing) were 0.3 μm in thickness. Isopressing at 125 or 135 MPa (after a 400 °C heat treatment) resulted in a reduction to 0.2 μm (after crystallisation at 700 °C), with no significant change up to the maximum pressure studied 200 MPa, Fig. 1. Numerous pores were present in the unpressed film, with the largest $\sim 70 \text{ nm}$ in size being located predominantly in the lower portion of the film adjacent to the film/substrate interface, Fig. 1a. A film pressed at 100 MPa showed similar porosity and thickness to an unpressed film. However, films pressed at 125–135 MPa were much more dense, exhibiting fewer pores and maximum pore dimensions were around half of those unpressed samples, Fig. 1b. There was little further change at higher pressures, Fig. 1c.

The P – E loops of films pressed under different pressing conditions are shown in Fig. 2. The unpressed film, Fig. 2a, showed a P – E hysteresis loop approaching saturation, with a remanent polarisation, P_r value of $26 \mu\text{C cm}^{-2}$. The film pressed at 100 MPa had a similar value of P_r to the unpressed film, but P_r increased to $34 \mu\text{C cm}^{-2}$ for a 125 MPa treatment, Fig. 2b, falling slightly

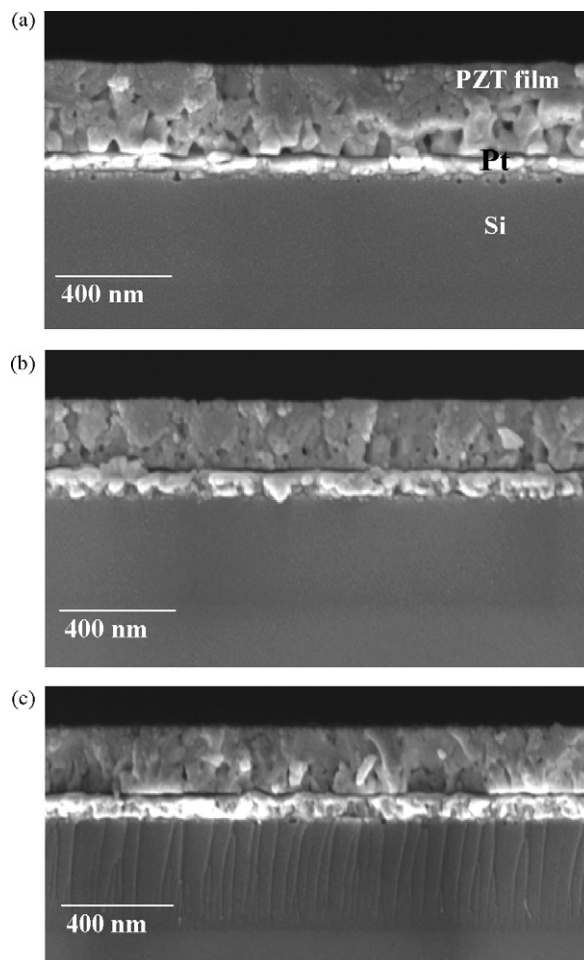


Fig. 1. Scanning electron micrographs of the cross-sections of the films: (a) without compaction; (b) pressed at 135 MPa and (c) pressed at 200 MPa.

to $31 \mu\text{C cm}^{-2}$ for 135 MPa, Fig. 2c. However, pressing at 150 MPa reduced P_r to $20 \mu\text{C cm}^{-2}$, a value lower than for an unpressed film. There was a further reduction to $16 \mu\text{C cm}^{-2}$ for a film pressed at 200 MPa, Fig. 2d. Values of P_r and corresponding values of coercive field, E_c , are plotted as a function of pressure in Fig. 3. The values of coercive field (E_c) depict a rising trend with increased compaction pressure. This was most noticeable above 125 MPa with E_c increasing from 92 to 105 kV cm^{-1} between 125 and 165 MPa. P – E loops were generally displaced along the field axis. This is a common feature in ferroelectric thin films, and has been attributed in the literature to internal bias fields, for example as a result of an asymmetric space–charge distribution associated with alignment of dipoles (self-polarisation) during cooling, or to asymmetry of top and bottom electrodes (Pt and Au in the present example) [11].

The conventional θ – 2θ XRD pattern for the unpressed film, Fig. 4, shows single-phase $\text{Pb}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3$. All the other films showed similar XRD patterns, but with evidence of slight changes in relative intensity of the PZT peaks. A bulk powder of this composition would show tetragonal symmetry but peak broadening occurs in thin film samples obscured any tetragonal peak splitting in the thin film XRD patterns, which appear pseudocubic. The XRD patterns of the films showed an enhancement of (1 1 1) peak intensity relative to a random powder pattern. Pole plots were used to examine the existence of (1 1 1) preferred orientation in the plane of the substrate. Because of the proximity of the dominant Pt (1 1 1) electrode peak to the PZT (1 1 1) peak, the extent of texture was investigated with respect to the PZT (2 0 0) peak ($2\theta = 45.38^\circ$) and correlations

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