Structural, electric and ferroelectric properties of PZT films obtained using oxide precursors

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Structural, electric and ferroelectric properties of PZT films obtained using oxide precursors

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Abstract. Ferroelectric thin films of PZT, with a Zr/Ti molar ratio of 53/47, were prepared by a method that uses oxides as precursors, and deposited on Pt/Si. Films of 0.5 μm thickness were obtained. Tetragonal and rhombohedral phases were identified as being present in these films. The dielectric constant (ε') and dissipation factor ($\tan\delta$) at a frequency of 100 kHz were 514 and 0.057, respectively. Capacitance–voltage characteristics were also measured. The ferroelectricity was confirmed by polarization–field hysteresis loops, with remanent polarization and coercive-field values of 4.9 μC cm^{-2} and 45.9 kV cm^{-1}, respectively.

Lead zirconate titanate, $PbZr_xTi_{1-x}O_3$ (PZT), is the most studied perovskite-type ferroelectric material—as bulk ceramic as well as thin films. PZT solid-solution ceramics are well known for their excellent piezoelectric, dielectric and pyroelectric properties [1]. The composition with $Zr/Ti = 54/46$ lies at the morphotropic phase boundary, which corresponds to a transition from tetragonal to rhombohedral structure [2]. At this phase boundary, most of the properties, such as the dielectric constant, piezoelectric coefficients and electromechanical coupling coefficient, show their maximum values [1]. Hence, the preparation of PZT thin films has been attracting practical interest [3].

For more than a decade, the fabrication of PZT films has been reported, using methods such as the electron beam evaporation [3], rf sputtering [4, 5] and sol–gel [6] techniques. Solution deposition enables better stoichiometric control of complex compositions to be achieved than other physical techniques such as rf sputtering, laser ablation [7] and chemical vapour deposition (CVD) [8]. The search for new routes for obtaining the solutions for film deposition remains an interesting subject; the aim is to achieve better stability of complex compositions and/or cheaper processing.

Very recently the preparation of PZT thin films using oxide precursors [9] was proposed. This method is a hybrid chemical method for ferroelectric thin-film preparation, based on a pre-calcination of oxides or carbonates. The method was successfully applied to prepare PZT thin films on fused quartz or Pt/Si substrates. The films showed good quality and homogeneity and a high degree of stoichiometry control [9]. In this paper, we report the structural, electrical and ferroelectric properties of PZT thin films obtained using oxide precursors, by a method that was described in our recent paper [9].

PZT films, with a Zr/Ti molar ratio of 53/47, were deposited on platinized silicon substrates (Pt/Si) by dip coating. The films were annealed at 300 °C for six hours, to remove residual solvents, and at 700 °C for two hours, for crystallization. The films obtained are about 0.5 μm

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thick. The structure of the films was examined by x-ray diffraction (XRD) analysis, using Cu Kα radiation.

The electrical properties include dielectric and capacitance–voltage (C–V) characteristics. The measurements were conducted in a metal–ferroelectric–metal (MFM) configuration. To measure the electrical properties, several electrodes of gold (0.3 mm in diameter) were deposited over an area of 2 cm $\times$ 2 cm on the films through a mask, to form MFM capacitors. The dielectric constant (ε'), dielectric loss factor (tan δ) and capacitance–voltage characteristics were measured with an HP 4194A impedance analyser. A Sawyer–Tower circuit at 300 Hz was used to measure the ferroelectric properties.

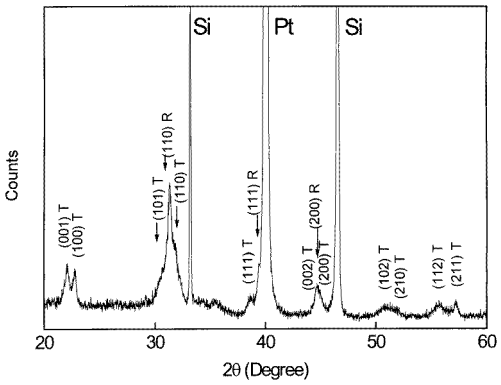

Figure 1. X-ray diffraction results for the PZT (Zr/Ti = 53/47) thin film, annealed at 700 °C for 2 h, on a Pt/Si substrate.

The as-deposited films, annealed at 350 °C for six hours, were confirmed to be amorphous by XRD. Figure 1 shows the XRD pattern of PZT film on Pt/Si substrate, fired at 700 °C for two hours. In this figure, we can identify the presence of a coexisting tetragonal and rhombohedral phases. The lattice constants a and c of PZT were calculated for the tetragonal phase using the (001), (002) and (200) peaks, and were found to be 3.99 and 4.10 Å ($c/a = 1.02$), respectively. This c/a ratio is very close to those reported for bulk PZT ceramics with the same composition [1] and PZT thin films produced by the sol–gel technique [6]. For the rhombohedral phase,

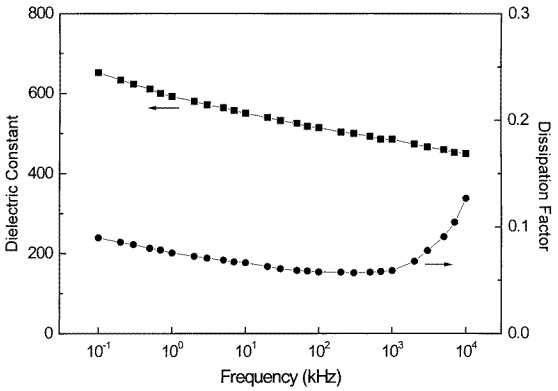

Figure 2. The dielectric constant and dissipation factor as a function of frequency for PZT film, annealed at 700 °C for 2 h.

we used the (110), (111) and (200) peaks, and obtained $a = 4.04$ Å and $90 - \alpha = 0.02^{\circ}$.

The dielectric behaviour of the PZT films, examined in terms of the dielectric constant and dissipation factor as functions of the measuring frequency, are summarized in figure 2 for films annealed at 700 °C for two hours. It may be seen that the films exhibit a slight frequency dependency, which is consistent with the expected normal behaviour. The dielectric constant and dissipation factor at a frequency of 100 kHz were 514 and 0.057, respectively. The value of the dielectric constant obtained here is slightly smaller than that of the corresponding sintered body with the same composition [1]. On the other hand, these results are consistent with other reports for thin films [10].

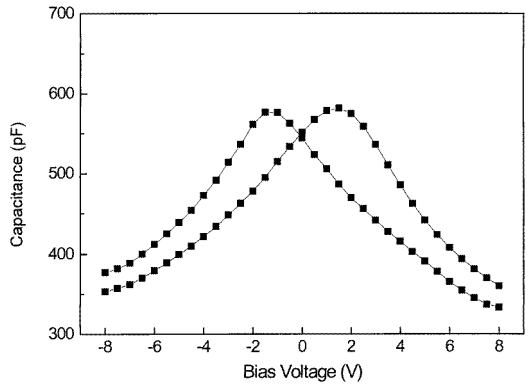

Figure 3. The C–V curve for PZT film, annealed at 700 °C for 2 h, on a Pt/Si substrate.

The bias dependence of the capacitance was also studied for films annealed at 700 °C for 2 h. A small ac signal of 10 mV amplitude and 100 kHz frequency was applied across the sample while the dc electric field was swept from positive bias to negative bias and back again. Figure 3 shows the C–V characteristic of the film in the MFM configuration. Two maxima, which are due to ferroelectric polarization reversals, are clearly seen in figure 3. The two observed maxima can be regarded as double the coercive field (E_c). From this figure, E_c was obtained as 29.4 kV cm^{-1}. Generally, the coercive fields determined from the C–V measurements were somewhat smaller than E_c determined from the hysteresis loop

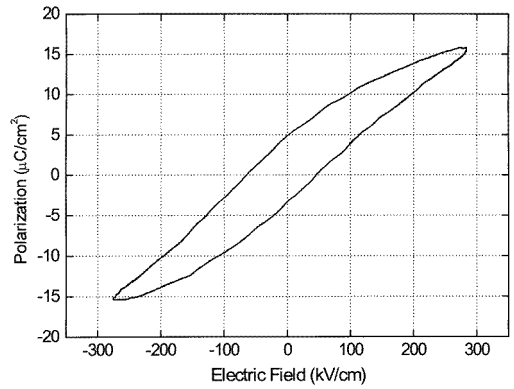

Figure 4. The hysteresis loop measured at 300 Hz for a PZT film 0.5 mm thick on a Pt/Si substrate.

measurements, due to the dependence of E_c on the applied voltage and frequency. In addition, the capacitance values of the different electrodes varied by less than 3%, indicating a good degree of uniformity of the thicknesses of the films.

Hysteresis loops were observed at room temperature, at 300 Hz. Figure 4 shows a typical P–E hysteresis loop for a film annealed at 700 °C for 2 h. The remanent polarization (P_r) and the coercive field (E_c) are 4.9 μC cm^{-2} and 45.9 kV cm^{-1}, respectively. For PZT films the values of P_r and E_c ranged from 1–7 μC cm^{-2} and 26–80 kV cm^{-1}, respectively, obtained by the sol–gel technique [6], or 3–30 μC cm^{-2} and 25–64 kV cm^{-1}, for films obtained by the dc magnetron sputtering technique [11]. In this work the observed slightly lower P_r and higher E_c may be associated with the smaller grain size in comparison with that of bulk ceramics [1].

In conclusion, PZT thin films were successfully deposited on Pt/Si substrates using the oxide precursor method. These films were characterized as regards their structural, electrical and ferroelectric properties. The results obtained are comparable with others results obtained from chemical processes.

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