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Journal of the European Ceramic Society 25 (2005) 2281–2284

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Fatigue properties of oriented PZT ferroelectric thin films

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Available online 30 March 2005

Abstract

Oriented PZT thin films with Zr/Ti ratio of 60/40 were prepared using a multi-target R.F. sputtering system. The films were (1 0 0) or (1 1 1) oriented when grown on $Pt/TiO_2/SiO_2/Si$ and exhibited *c*-axis epitaxial microstructure when deposited on Pt/MgO. Electrical measurements were performed in order to investigate the fatigue properties of the films. Fatigue characteristics of the Pt/PZT/Pt capacitors were found to be strongly dependent on their crystalline orientation: (1 1 1) and (0 0 1) oriented films exhibited poor fatigue endurance unlike (1 0 0) oriented films that did not fatigue. Lastly, almost full recovery of polarisation was obtained for *c*-axis epitaxial films while (1 1 1) oriented films showed only partial restoration.

Keywords: Films; Ferroelectric properties; Fatigue; PZT

1. Introduction

PZT is an extensively studied material since its ferroelectric properties offer a great promise for various applications such as ferroelectric non-volatile memories (NVFRAM).[1] An important particularity of ferroelectric materials is that electrical properties depend on the crystallographic orientation of the films.[2,3] By monitoring the orientation of the PZT film, it is possible to optimise some properties of the material (polarisation, dielectric permittivity, piezoelectric coefficient). Moreover, some authors have reported that film orientation has a strong influence on polarisation fatigue.[4–6] Fatigue is an important failure mechanism of ferroelectric thin films, which manifests itself by a progressive reduction of the amount of switched charges with increasing polarisation reversals. Detailed information about this phenomenon, including experimental data and models, can be found in a recent review by Tagantsev et al.[7] Despite the large number of paper dedicated to this subject, the physical origin of fatigue is still under debate. In this paper, highly oriented PZT thin films have been grown in situ, without any post-annealing treatment, and the influence of orientation on the fatigue properties has been investigated. Experimental results on the restoration of polarisation after fatigue are also presented.

2. Experimental

Oriented $Pb(Zr_{0.6}\ Ti_{0.4})O_3$ films were grown in situ at 500–550 °C by RF sputtering on both Pt/MgO and $Pt/TiO_2/SiO_2/Si$ substrates. The Pt layer exhibited (1 1 1)-oriented microstructure when prepared on Si/SiO_2 substrate, while (1 0 0) orientation was obtained when deposited on MgO substrate. A thin TiO_x layer was deposited on the platinum electrode prior to PZT by sputtering a Ti target. In previous reports,[8–10] we demonstrated that this thin TiO_x layer not only promoted the crystallisation of PZT film but also allowed the control of the orientation by monitoring the $O_2/(Ar+O_2)$ ratio in the plasma gas during Ti deposition. With regard to Pt/Si substrate, when Ti was sputtered under a pure argon ambience, highly (1 0 0) textured PZT films were grown, whereas highly (1 1 1) textured ones crystallised when Ti was deposited in a mixed argon-oxygen atmosphere. Concerning Pt/MgO substrate, *c*-axis epitaxial growth may be achieved by controlling the $O_2/(Ar+O_2)$ ratio in the plasma gas during the deposition of both TiO_x and PZT films. It must be mentioned that the PZT film structure was tetragonal on Pt/MgO substrate. The presence of such tetragonal phase within a re-

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doi:10.1016/j.jeurceramsoc.2005.03.046

gion of Zr/Ti composition where a rhomboedral structure is expected was already reported by Oh et al.[11] and may arise from strains induced by the substrate.

Crystallographic properties of PZT films were examined by a Seifert X-ray Diffractometer (XRD) using CuK_α radiation. The composition of the films was investigated by energy dispersive spectroscopy (EDS) analysis. To characterise the ferroelectric properties of PZT thin films from an electrical point of view, 250 μm × 250 μm square capacitors were designed by UV photolithography using a metallic shadow mask. Pt was sputtered at room temperature on film surface and top contacts were then patterned by lift off. Electrical measurements were performed using the radiant technology precision workstation ferroelectric tester (RT) and a conventional Sawyer-Tower circuit (S-T).

3. Results and discussion

The X-ray diffraction patterns of the PZT films deposited on $Pt/TiO_2/SiO_2/Si$ and Pt/MgO substrates are shown in Fig. 1. It can be seen that highly oriented PZT films were obtained. The polarisation hysteresis loops measured with an applied voltage of 6 V on 200 nm thick PZT films are shown in Fig. 2. As expected, ferroelectric properties depend on crystallographic orientation of the PZT film. Fig. 3 shows results of fatigue test performed on these PZT films. The normalised remnant polarisation P_r is plotted as a function of the number of cycles. During the fatigue test, the films were subjected to bipolar rectangular switching pulses of frequency 100 kHz and amplitude 6 V. Both (1 1 1) and (0 0 1) oriented films were found to be very prone to fatigue. A reduction of more than 80% of the remnant polarisation was obtained after only 10^6 cycles for (1 1 1) oriented films and 10^9 cycles for (0 0 1) ones. These losses of remnant polarisation are also visible in the hysteresis loops after fatigue test (Fig. 2). The decrease of the remnant polarisation is associated with a tilt of the loop and a reduction of both maximum polarisation and coercive fields. On the contrary, the (1 0 0)-textured films did not show

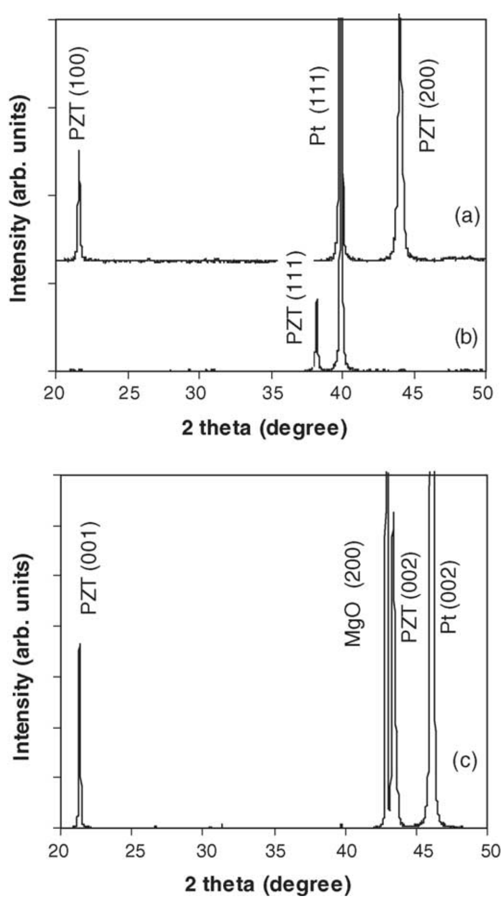

Fig. 1. XRD patterns of PZT (60/40) films with different orientations: (1 0 0) or (1 1 1) on $Pt/Ti/SiO_2/Si$ substrate, respectively (a) and (b), and (0 0 1) on Pt/MgO substrate (c).

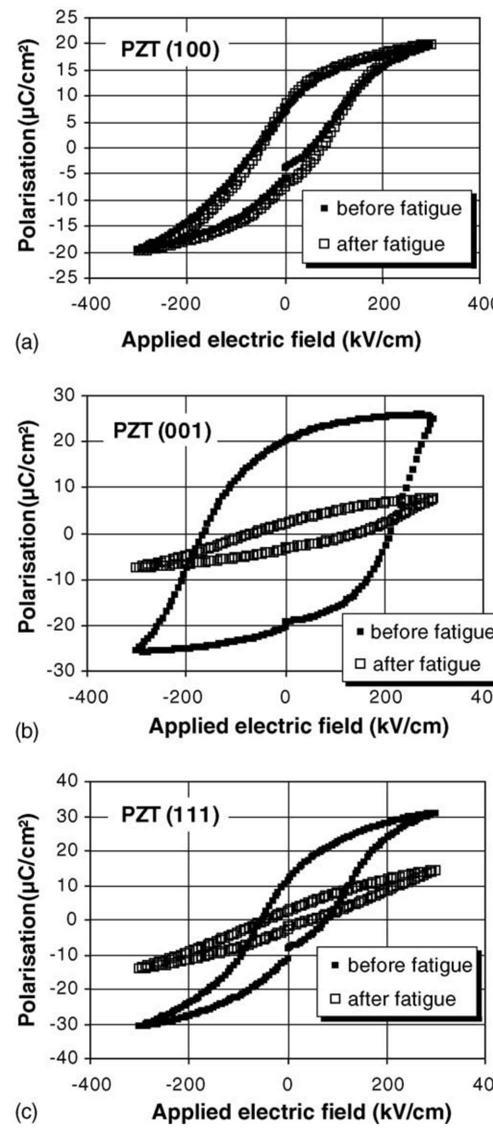

Fig. 2. Polarisation hysteresis loops (before fatigue and after 10^{10} cycles) of PZT (60/40) thin films as a function of crystalline orientation. (a): PZT (1 0 0), (b): PZT (0 0 1) and (c): PZT (1 1 1).

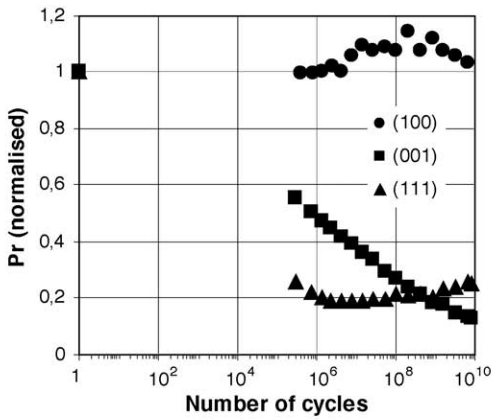

Fig. 3. Dependence of polarisation fatigue on the orientation of PZT thin films. $F = 100$ kHz and $V = 6$ V.

any noticeable fatigue up to 10^{10} cycles as confirmed by the polarisation loop after fatigue (Fig. 2). These results clearly demonstrate that fatigue behaviour is strongly related to the crystallographic orientation as previously reported for Ti rich PZT films[4] and for PZT films prepared by sol–gel process.[6]

It is well known that ferroelectric properties of fatigued ferroelectric capacitors can be refreshed by applying DC electric field,[12,13] heat treatment[14] or UV light illumination.[15] In our case, we observed different restoration levels depending on the film texture. *C*-axis epitaxial PZT films were partially restored after recording hysteresis loops with the RT ferroelectric tester at a voltage (15 V) larger than that of the fatigue test. Furthermore, almost full restoration of P_r and P_{max} was possible by repeated cycles at 15 V with the Sawyer-Tower circuit driven by a sine wave (Fig. 4). However, the restoration of polarisation was associated with an increase of coercive fields (E_c^+ and E_c^-). This could be directly related to the existence of an internal field due to space charges trapped at electrode–PZT interfaces. It should be noted that repeated recordings of hysteresis loops at 15 V with the RT ferroelectric tester did never allow full recovery of polarisation

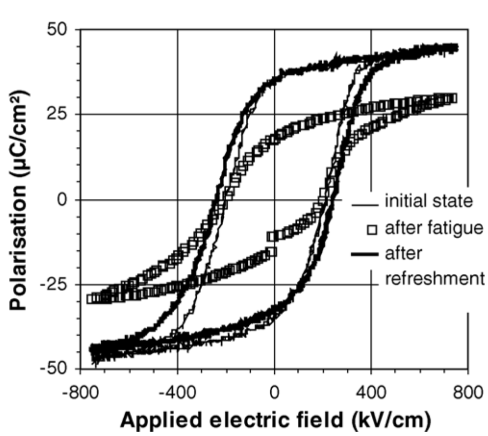

Fig. 4. Hysteresis loops of the (001) oriented PZT film. (—) virgin state, (□) after 10^{10} switching cycles, (▬) after 10^{10} switching cycles and a subsequent cycling with the Sawyer-Tower circuit at 15 V.

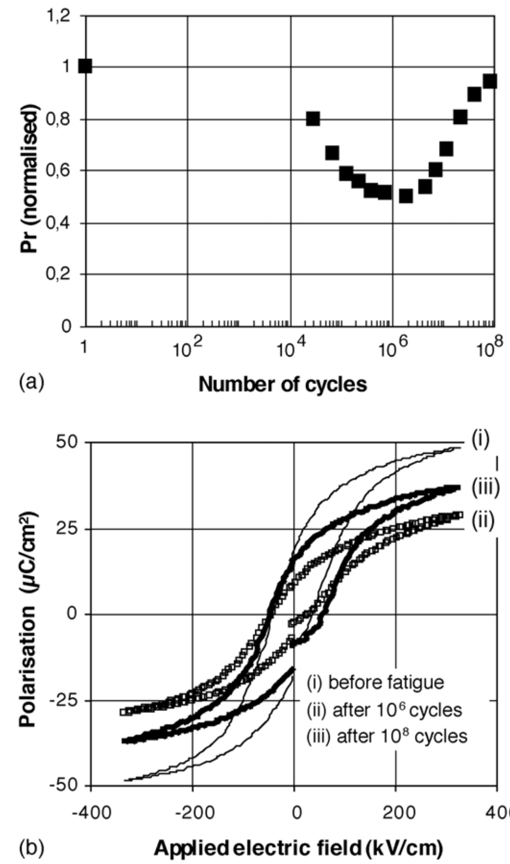

Fig. 5. Restoration of the remnant polarisation for a 450 nm thick (1 1 1)-oriented PZT film fatigued at 10 kHz with a bipolar square signal: (a) self-recovery effect observed during fatigue test, (b) hysteresis loops: (i) before fatigue, (ii) after 10^6 cycles and (iii) after 10^8 cycles.

as with the S-T circuit. This behaviour may arise from the different nature of the two circuits. In the case of (1 1 1) oriented films, partial recovery of ferroelectric properties could also be obtained after application of a voltage above that of the fatigue test (field induced recovery effect). But we never obtained full recovery of polarisation as for (0 0 1)-oriented films. Restoration of remnant polarisation in the course of fatigue test (self-recovery effect), similar to that reported by Colla et al.,[12] was also observed under particular conditions (Fig. 5a). In that case, full restoration of remnant polarisation was possible whereas maximum polarisation remained diminished as illustrated in Fig. 5b. Lastly, it must be precised that such self-recovery effect was preferentially observed for thicker films (450 nm) and occurred preferentially when a bipolar square wave was used as a fatigue signal.

4. Conclusions

The effects of crystallographic orientation on the ferroelectric properties of PZT thin films have been investigated. Experimental results clearly indicate that polarisation fatigue depends on the film orientation. The (1 0 0) oriented PZT film exhibits very good fatigue endurance unlike both (1 1 1) and (0 0 1) oriented films that present drastic polarisation suppression under electrical stress. Moreover, restoration of polarisation, more or less pronounced depending on film orientation and fatigue test parameters, was possible during or after fatigue test. As a result of this study, it can be concluded that understanding of physical origin of fatigue may be achieved providing further investigations to be carried out on purely oriented films.

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