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Effect of fatigue on the pyroelectric and dielectric properties of PZT films

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Abstract

Sol-gel derived lead zirconate titanate ($PbZr_{0.52}Ti_{0.48}O_3$) films of thickness 1 μm were deposited on $RuO_2/SiO_2/Si$ and $Pt/Ti/SiO_2/Si$ substrates. The crystallization of the films was studied by X-ray diffraction. The pyroelectric coefficient and dielectric permittivity of the PZT films were also investigated. It is well known that the use of oxide electrodes can reduce fatigue in PZT thin films. In this work, the effect of fatigue on the dielectric and pyroelectric properties of 1 μm thick PZT films was studied by comparing these properties before and after fatigue tests. As a fatigued film has lower switchable polarization, this study will reveal the correlation between dielectric and pyroelectric properties of PZT films and switchable polarization. © 2001 Published by Elsevier Science Ltd.

Keywords: Dielectric properties; Fatigue; Pyroelectric coefficient; PZT

1. Introduction

Recently, there has been growing interest in using lead zirconate titanate (PZT) ferroelectric thin films in various fields of application, such as nonvolatile memories, pyroelectric detectors, and microelectromechanical systems (MEMS).[1,2] However, the problem of fatigue that leads to a significant reduction in switchable polarization often limits the applications of the films. A lot of work have been focused on investigating the mechanisms of fatigue and studying ways to improve the fatigue resistance of the PZT thin films. Domain pinning or freezing was the widely suggested mechanisms for the suppression of switchable polarization leading to fatigue.[3–5] It has been shown that the use of conductive oxide electrodes, such as RuO_2 [6] and $SrRuO_3$ [7] could improve the fatigue resistance substantially. However, there are few studies of the effect of continuous polarization switching on the piezoelectric coefficient of PZT thin films. Kholkin et al.[5] have shown that the longitudinal piezoelectric coefficient d_{33} of a fatigued PZT thin film became smaller, and the piezoelectric hysteresis loop shifted upwards resulting from the pinning of ferroelectric domains in a preferred orientation. In this work, we have studied the pyroelectric and dielectric properties in sol-gel derived PZT films, and their correlation with the switchable polarization. The influence of using different electrode materials, ruthenium dioxide (RuO_2) and platinum (Pt), has also been investigated.

2. Experimental

RuO_2 bottom electrode of thickness 150 nm was deposited on SiO_2/Si substrates at 350°C by reactive rf magnetron sputtering in a gas mixture of argon and oxygen ($Ar/O_2 = 50/50$), whereas Pt/Ti bottom electrode of thickness 180 nm/20 nm was deposited by dc magnetron sputtering in a pure Ar atmosphere. The PZT films were prepared using a sol-gel method. A PZT precursor solution ($Zr/Ti = 52/48$), with 10% excess Pb, was prepared from lead acetate trihydrate $Pb(OAc)_2{\cdot}3H_2O$, titanium isopropoxide $Ti(O\text{-}i\text{-}Pr)_4$, and zirconium *n*-butoxide $Zr(O\text{-}n\text{-}Bu)_4$. The precursor solution was spin

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coated on $RuO_2/SiO_2/Si$ and $Pt/Ti/SiO_2/Si$ substrates to give films of thickness about 100 nm, which were then pyrolyzed at 400°C for 10 min. After the deposition of four layers, the films were annealed in an oxygen atmosphere at 550°C for 3 min in a rapid thermal processor (RTP). By repeating the process a few times, PZT films of thickness 1 μm were obtained. The films were then annealed at 650°C for 1 h in a furnace. For electrical measurements, a top electrode of the same materials as the bottom electrode was deposited by sputtering. The diameter of the top electrode was 1 mm.

Crystalline structure of the films was studied using X-ray diffractometer (Philips X'pert XRD system) with Ni filtered CuK_α radiation. The dielectric permittivity ε_r at 1 kHz was evaluated using an impedance analyzer (HP 4194A). A dynamic method was used to measure the pyroelectric coefficient at room temperature.[8] The polarization hysteresis loop and fatigue characteristic were evaluated using a RT66A ferroelectric tester (Radiant Technology Ltd). In the fatigue test, the film sample was subjected to bipolar square switching pulses of frequency 25 kHz and amplitude 18 V, which was sufficiently high to completely switch the polarization. After subjected to different switching cycles, the switchable polarization ($P^*-P^\wedge$, measured using the RT66A tester), dielectric permittivity and pyroelectric coefficient of the film sample were determined. The switched polarization (P*) and the non-switched polarization ($P^\wedge$) were determined from a pulse polarization test using the waveform shown in Fig. 1. P^* was measured by subjecting the film sample to two triangular pulses of opposite polarities, and $P^\wedge$ was measured after subjecting the film to two triangular pulses of the same polarity.

3. Results and discussion

The X-ray diffraction patterns of the PZT thin films deposited on $RuO_2/SiO_2/Si$ and $Pt/Ti/SiO_2/Si$ substrates are shown in Fig. 2. It should be noted that the processing conditions for preparing PZT films on different substrates are identical. It can be seen that no pyrochlore or PbO_x phases are observed in these films. Due to the high nucleation site density of the perovskite phase, the (100) plane of which the activation energy is the lowest grows more easily and faster, and becomes the dominant orientation in the PZT/Pt film.[9] The PZT/RuO_2 film shows random orientation. This may be due to the smoother surface and consequently the lower nucleation site density of the perovskite phase on RuO_2 electrode.[9]

The polarization hysteresis loops obtained from the $RuO_2/PZT/RuO_2$ and Pt/PZT/Pt films are shown in Fig. 3. The remanent polarization P_r of the as-prepared $RuO_2/PZT/RuO_2$ film ($P_r = 20.3$ μC/cm^2) is slightly lower than that of the Pt/PZT/Pt film ($P_r = 22.5$ μC/cm^2), while the coercive field E_c is about 25% lower in the $RuO_2/PZT/RuO_2$ film (32 kV/cm vs 42 kV/cm). Fig. 4 shows the results of bipolar fatigue test performed on the $RuO_2/PZT/RuO_2$ and Pt/PZT/Pt films, in which the normalized switchable polarization ($P^*-P^\wedge$) is plotted as a function of switching cycles. Because of the use of oxide electrodes, the $RuO_2/PZT/RuO_2$ film exhibits better resistance to polarization fatigue than the Pt/PZT/Pt films. The switchable polarization of the $RuO_2/PZT/RuO_2$ film remains almost unchanged up to 10^7 switching cycles, and then decreases by about 8% after 4×10^9 switching cycles. On the contrary, the Pt/PZT/Pt film starts to degrade after only 10^5 switching cycles, and has a 33% drop in the switchable polarization after 4×10^9 switching cycles. These losses of switchable polarization are also reflected in the polarization hysteresis loops (Fig. 3). While little change is observed for the fatigued $RuO_2/PZT/RuO_2$ film, the shape of the hysteresis loop of the fatigued Pt/PZT/Pt

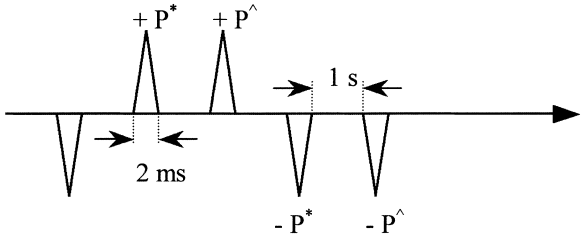

Fig. 1. Schematic of the pulse train used to measure the pulse polarization.

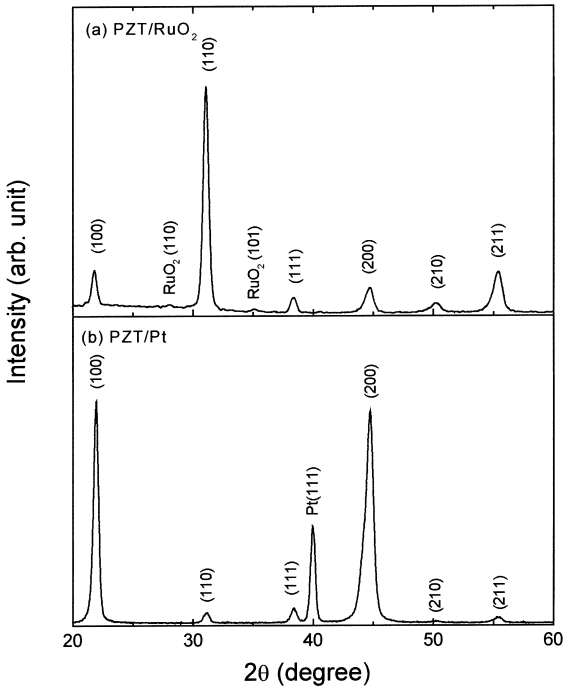

Fig. 2. XRD patterns of PZT films deposited on (a) $RuO_2/SiO_2/Si$ and (b) $Pt/Ti/SiO_2/Si$ substrates.

films has a noticeable change, with about 25% decrease in the remanent polarizaton and 15% increase in the coercive field. Since the polarization hysteresis loop is usually measured at a lower frequency (~2 Hz), the observed remanent polarization would include the charge due to leakage current. Therefore, the difference between P^* and $P^\wedge$ which are measured at a much faster frequency (~500 Hz) are usually used to represent the switchable polarization.

The room temperature pyroelectric coefficients of the as-prepared RuO_2/PZT/RuO_2 and Pt/PZT/Pt films are 138 μC/m^2 K and 145 μC/m^2 K, respectively. The variations of the normalized pyroelectric coefficient with switching cycles for both samples are shown in Fig. 5. It can be seen that the fatigue of the pyroelectric property follows almost the same way as that of polarization, indicating that the pyroelectric coefficient is greatly dependent on the switchable polarization. It is also observed that if the fatigued Pt/PZT/Pt films are subsequently poled by an ac field, their pyroelectric coefficients are independent of the direction of the poling field. This shows that if polarization domains are frozen or pinned in the film during the fatigue process, they have no preferred orientation and no contribution to the observed pyroelectric coefficient.

The variations of the dielectric permittivity with switching cycles for both samples are shown in Fig. 6. The dielectric permittivity of the as-prepared RuO_2/PZT/RuO_2 film ($\varepsilon_r = 1110$) is about 10% smaller than that of the as-prepared Pt/PZT/Pt film ($\varepsilon_r = 1220$). This may arise from the larger population of the (100)

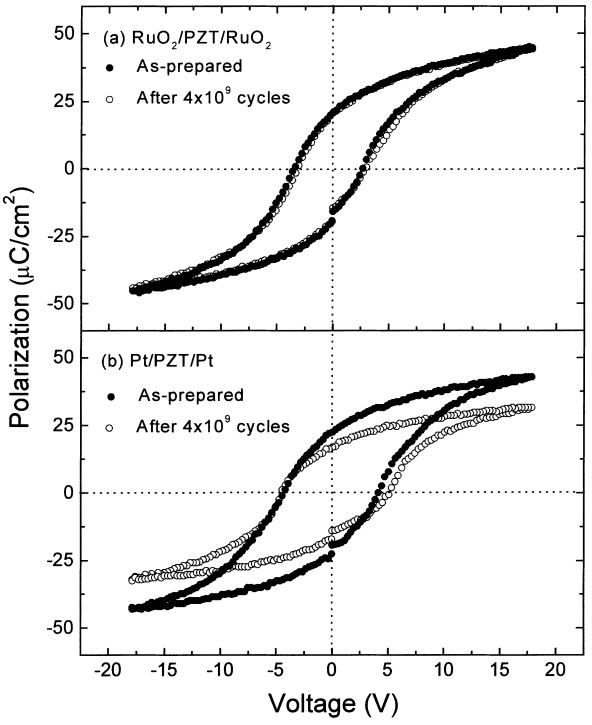

Fig. 3. Polarization hysteresis loops of (a) RuO_2/PZT/RuO_2 and (b) Pt/PZT/Pt films. The symbols ● and ○ denote the loops obtained before and after 4×10^9 switching cycles, respectively.

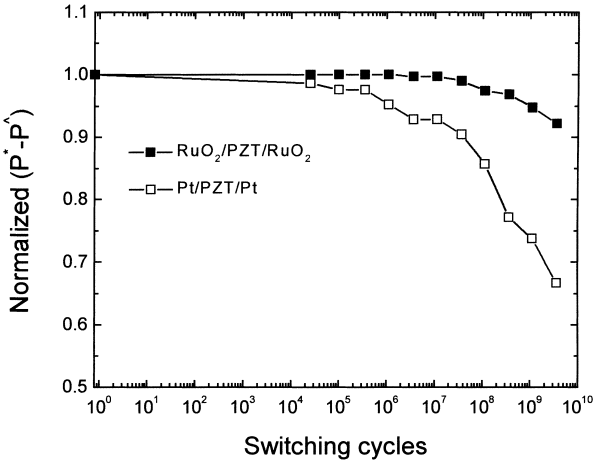

Fig. 4. Normalized switchable polarization ($P^*-P^\wedge$) as a function of switching cycles. Data: ■, RuO_2/PZT/RuO_2 film; □, Pt/PZT/Pt film.

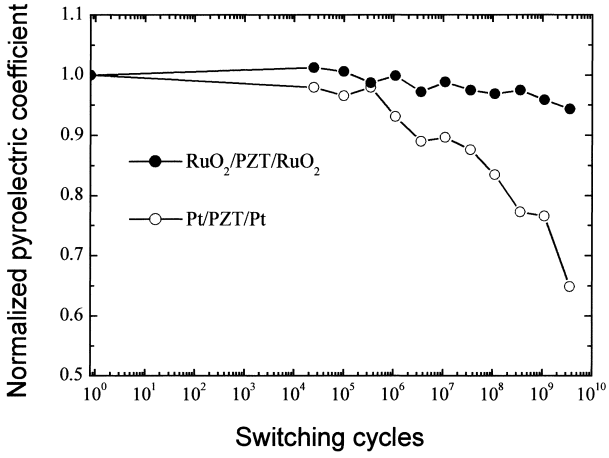

Fig. 5. Normalized pyroelectric coefficient as a function of switching cycles. Data: ●, RuO_2/PZT/RuO_2 film; ○, Pt/PZT/Pt film.

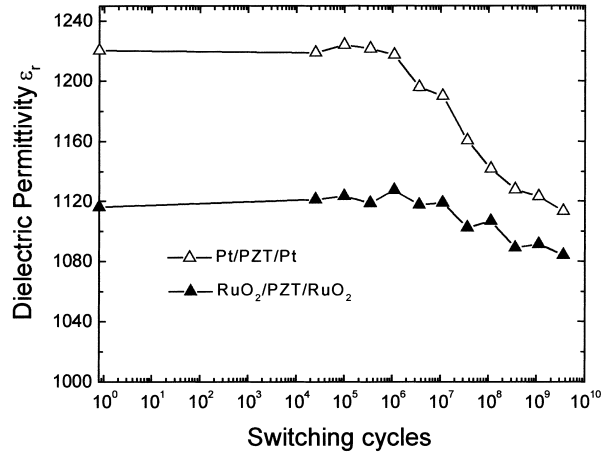

Fig. 6. Dielectric permittivity as a function of switching cycles. Data: ●, RuO_2/PZT/RuO_2 film; △, Pt/PZT/Pt film.

domain in the Pt/PZT/Pt film (Fig. 2), since the dielectric permittivity along the *a*-axis of a highly tetragonal PZT ceramic is larger than that along the *c*-axis.[10] It is interesting to note that both samples exhibit fatigue degradation in dielectric permittivity, with degradations smaller than those in switchable polarization and pyroelectric coefficient. This indicates that the suppression of the switchable polarization may not arise from the locking of the ferroelectric domain walls in the film by the mobile charged defects as proposed by Warren et al.[11] and other workers. The observed dielectric permittivity in ferroelectric materials consists of the contributions from the dielectric properties of the lattice and the bending motions of the ferroelectric domain walls.[12] Although the locked domain walls do not contribute to the polarization switching, they are still expected to be excited in bending motion under a small ac field during the dielectric permittivity measurement. In addition to the improved fatigue properties of the PZT films using oxide electrodes, it is believed that the inhibition of the nucleation or the locking of the opposite polarization seeds at the electrode–ferroelectric film interfaces would be the mechanism for the suppression of the switching polarization.[13] One possible scenario, which is not verified yet, is that during the continuous switching process, charged defects such as oxygen vacancies ($V\ddot{o}$) migrate and accumulate at the PZT/Pt interfaces, leading to inhibition of the domain seeds. When all the local seeds are inhibited, the grains or regions including several grains become ferroelectrically dead, resulting in a decrease of polarization domains, and consequently switchable polarization, pyroelectric coefficient, and dielectric permittivity. If oxide electrode is used, it may act as a sink for the oxygen vacancies and then hinder the inhibition of the domain seeds.

4. Conclusion

This study reveals the fatigues of pyroelectric and dielectric properties in sol-gel derived PZT films with Pt and RuO_2 electrodes. The RuO_2/PZT/RuO_2 film exhibits better fatigue resistance not only in polarization but also in pyroelectric and dielectric properties compared to the Pt/PZT/Pt film. With the suppression of the switchable polarization, the pyroelectric coefficient of the RuO_2/PZT/RuO_2 and Pt/PZT/Pt films decreases by almost the same fraction as the polarization (by 5 and 35%, respectively) after 4×10^9 switching cycles. The fatigue degradation in dielectric permittivity suggests that the suppression of the switchable polarization should not arise from the locking of the ferroelectric domain walls in the film by the mobile charged defects. It is suggested to be due to the decrease in polarization domains resulting from the inhibition of the domain seeds at the electrode-film interface.

Acknowledgements

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References

1. Scott, J. F. and Araujo, C. A., Ferroelectric memories. *Science*, 1989, **246**, 1400–1405.
2. Muralt, P., Ferroelectric thin films for micro-sensors and actuators: a review. *J. Micromech. Microeng.*, 2000, **10**, 136–146.
3. Colla, L., Hong, S., Taylor, D. V., Tagantsev, A. K. and Setter, N., Direct observation of region by region suppression of the switchable polarization (fatigue) in Pb(Zr,Ti)O-3 thin film capacitors with Pt electrodes. *Appl. Phys. Lett.*, 1998, **72**, 2763–2765.
4. Gruverman, A., Auciello, O. and Tokumoto, H., Nanoscale investigation of fatigue effects in Pb(Zr,Ti)O-3 films. *Appl. Phys. Lett.*, 1996, **69**, 3191–3193.
5. Kholkin, A. L., Colla, E. L., Tagantsev, A. K. and Taylor, D. V., Fatigue of piezoelectric properties in Pb(Zr,Ti)O-3 films. *Appl. Phys. Lett.*, 1996, **68**, 2577–2589.
6. Tuttle, B. A., Headley, T. J., Al Shareef, H. N., Voigt, J. A., Rodriguez, M., Michael, J. and Warren, W. L., Microstructure and 90 degrees domain assemblages of Pb(Zr,Ti)O-3//RuO2 capacitors as a function of Zr-to-Ti stoichiometry. *J. Mater. Res.*, 1996, **11**, 2309–2317.
7. Foster, C. M., Bai, G. R., Csencsits, R., Vetrone, J., Jammy, R., Wills, L. A., Carr, E. and Amano, J., Single-crystal Pb(ZrxTi1-X) O-3 thin films prepared by metal-organic chemical vapor deposition: systematic compositional variation of electronic and optical properties. *J. Appl. Phys.*, 1997, **81**, 2349–2357.
8. Dias, C., Simon, M., Quad, R. and Das-Gupta, D. K., Measurement of the pyroelectric coefficient in composites using a temperature-modulated excitation. *J. Phys. D*, 1993, **26**, 106–110.
9. Kim, S. H., Hong, J. G., Gunter, J. C., Lee, H. Y., Streiffer, S. K. and Kingon, A., The effect of RuO2/Pt hybrid bottom electrode structure on the microstructure and ferroelectric properties of sol-gel derived PZT thin films. *Mater. Res. Soc. Symp. Proc.*, 1998, **493**, 131–136.
10. Kohli, M., Muralt, P. and Setter, N., Removal of 90 degrees domain pinning in (100) Pb(Zr0.15Ti0.85)O-3 thin films by pulsed operation. *Appl. Phys. Lett.*, 1998, **72**, 3217–3219.
11. Warren, W. L., Dimos, D., Tuttle, B. A., Nasby, R. D. and Pike, G. E., Electronic domain pinning in Pb(Zr,Ti)O3 thin-films and its role in fatigue. *Appl. Phys. Lett.*, 1994, **65**, 1018–1120.
12. Colla, E. L., Taylor, D. V., Tagantsev, A. K. and Setter, N., Discrimination between bulk and interface scenarios for the suppression of the switchable polarization (fatigue) in Pb(Zr,Ti)O-3 thin films capacitors with Pt electrodes. *Appl. Phys. Lett.*, 1998, **72**, 2478–2480.
13. Colla, E. L., Tagantsev, A. K., Taylor, D. V. and Kholkin, A. L., Fatigued state of the Pt–PZT–Pt system. *Integr. Ferroelectr.*, 1997, **18**, 19–28.