

Ferroelectric properties of $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3/\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3/(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ thin films with platinum electrodes

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Multilayered $\text{Pt}/(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3/\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3/(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3/\text{Pt}$ (BST/PZT/BST) thin films with different thicknesses of the BST layers were prepared by the pulsed-laser deposition method. The existence of a BST layer between the PZT and Pt electrode can greatly improve the fatigue properties of the PZT film. However, the heterostructure with thicker BST layers exhibits lower remnant polarization because of a lower electric field applied on the PZT layer. So, the thickness of BST layers should be decreased to decrease the working voltage of the multilayered film. A heterostructure with very thin BST layers (thickness ~ 7.5 nm) has good ferroelectric properties, such as high remnant polarization and rare fatigue resistance after 10^{10} switching cycles. A possible reason for the effect of BST is that the BST layer can absorb oxygen vacancies or other point defects from the PZT layer and greatly improve its fatigue properties. © 2003 American Institute of Physics. [DOI: 10.1063/1.1583137]

$\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) thin films have attracted the attention of many researchers for they can be used in nonvolatile ferroelectric random access memory (NVFRAM). However, a major problem with PZT-based memories is fatigue. Although the fatigue problem has been solved with the use of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) as Pt/SBT/Pt capacitor-based NVFRAMs and “smart cards” based on SBT-NVRAMs are already in the market,¹ there is still work needed to optimize PZT-based capacitors for integration into commercial NVFRAMs,^{1–4} since PZT has some advantages, such as a lower annealing temperature, simpler crystal structure, etc. Fatigue refers to the gradual reduction of switchable polarization after repeated alternating voltage pulses or switching cycles are applied to the sample. PZT thin films with Pt electrodes always have apparent fatigue after 10^8 switching cycles.² Although oxide electrodes can eliminate fatigue from PZT capacitors,^{1,5} a structure with Pt electrodes is more convenient for integration. In this letter, we report another structure of ferroelectric thin films—multilayered $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3/\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3/(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ (BST/PZT/BST) thin films with Pt electrodes, which show rare fatigue properties even after 10^{10} switching cycles. Since a BST film has the same perovskite structure and approximately the same annealing temperature as PZT, such a device can be easily integrated.

The fatigue of PZT thin films with Pt electrodes has been considered to be due to the pinning of oxygen vacancies or other charged point defects to ferroelectric domain walls.¹ As

explained in our prior paper,⁶ oxygen vacancies and other point defects in PZT thin films always move toward electrodes and accumulate near the Pt electrodes after some switching cycles due to the existing of an internal electric field in the Schottky barrier. Therefore, fatigue is induced by the dense oxygen vacancies or point defects near the interface. However, as for the PZT films with oxide electrodes, the oxygen vacancies moving to the electrodes can diffuse into the electrodes, thus few oxygen vacancies accumulate near the electrodes. This is the reason why PZT thin films with oxide electrodes have rare fatigue. In an effort to reduce the density of oxygen vacancies in the bulk of PZT and improve the fatigue properties, we have tried a different method: Adding BST layers between the Pt electrodes and the PZT film to absorb the oxygen vacancies from PZT thin film. So, it can be anticipated that the films would show good fatigue properties.

The films have a sandwich structure of BST/PZT/BST. At room temperature, BST film is in a paraelectric phase with a relatively high dielectric permittivity.⁷ When bias voltage is applied on the film, the three layers (BST, PZT, BST) have the same value of polarization for they are in series connection. The PZT layer is easier to be polarized or switched since the polarization in PZT is achieved by the motion of ferroelectric domain walls or the rotation of polar domains while it is different in BST for BST is in paraelectric phase. So, the electric field in the BST layers should be higher than that in the PZT layer since the same polarization should be achieved. Therefore, only if the BST layers are very thin, the voltage can be predominantly applied on the PZT layer, which is essential to the working voltage of this

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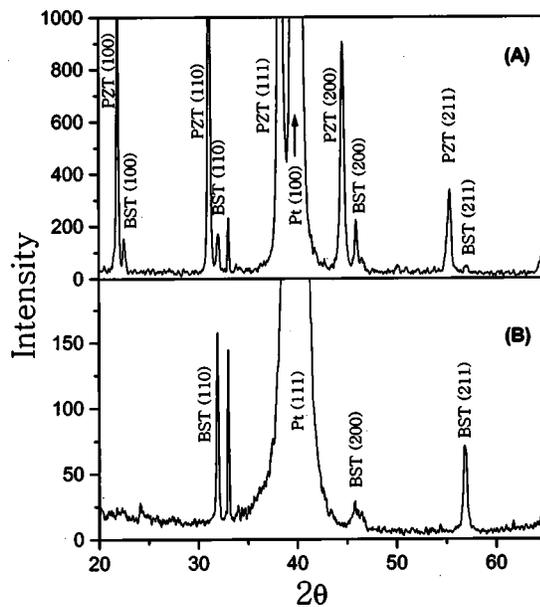


FIG. 1. XRD patterns (θ - 2θ scan, Cu $K\alpha$ radiation) (A) For BST/PZT/BST multilayered film with the thickness of BST layer: 30 nm and PZT layer: 600 nm, respectively, (B) BST layer on Pt electrode. The BST thickness is 50 nm.

multilayered ferroelectric capacitor. We have prepared such thin films with different BST thicknesses to find the optimum BST film thickness for a PZT-based capacitor.

The multilayered BST/PZT/BST thin films were grown on Pt/Ti/SiO₂/Si substrates at 550 °C using the pulsed-laser deposition method in 200 mTorr of oxygen. We used a KrF excimer laser (Lambda Physik Compex 205, $\lambda = 248$ nm) to ablate the PZT target (with the stoichiometry of 10% lead exceeded). The thickness of the PZT layer was 600 nm and the thickness of the BST layers was 30 nm, 15 nm, or 7.5 nm, measured by using cross section samples analyzed in a scanning electron microscope (SEM). The structure and morphology of the films were characterized by x-ray diffraction (XRD) and SEM analysis, respectively. Pt top electrodes were deposited on the films by rf magnetron sputtering through a shadow mask. The area of the top Pt electrode is 3.1×10^{-4} cm². The ferroelectric properties of the thin films were measured with a RT66A ferroelectric tester. The XRD patterns of the multilayered thin film with a BST layer are shown in Fig. 1(a), and the XRD patterns of a single BST layer on top of the bottom Pt electrode are shown in Fig. 2(b). The PZT layer is mainly (111) oriented and the BST layer has no preferred orientation.

The hysteresis loops of Pt/PZT/Pt and Pt/BST/PZT/BST/Pt capacitors with different thicknesses of BST layers are shown in Fig. 2. With the decrease of the thickness of the BST layer, the remnant polarization of PZT increases. These results indicate that the high polarization of such a device only can be achieved on the condition that BST layers are very thin. As shown in Fig. 2(d), the sample with the BST layer thickness of 7.5 nm can be polarized to a high value that is almost equal to the value of the pure PZT film shown in Fig. 2(a). However, the coercive field is two times higher than that of the PZT film. Because the coercive field is very

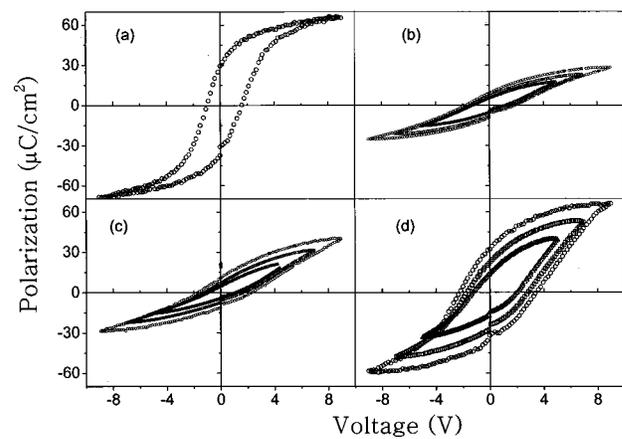


FIG. 2. The hysteresis loops of PZT film and multilayered BST/PZT/BST films with different thicknesses: (a) PZT and 600 nm, (b) BST/PZT/BST, BST: 30 nm and PZT: 600 nm, (c) BST/PZT/BST, BST: 15 nm and PZT: 600 nm, and (d) BST/PZT/BST, BST: 7.5 nm and PZT: 600 nm.

sensitive to the physical properties of the interfaces between the electrodes and film,^{8,9} we assume one possible reason for the very high coercive field is the more complicated interfaces between the film and electrodes. Another reason is that the two BST layers in series connection with the PZT layer may change the shape of the hysteresis loop, and the coercive field as well.

Figure 3 shows the fatigue properties of the PZT- and BST/PZT/BST-based capacitors. The measurement frequency is 2.5×10^4 Hz and the applied voltage is 9 V. The PZT capacitor has apparent fatigue after 10^9 cycles, while the BST/PZT/BST-based capacitor only shows little fatigue even after 10^{10} cycles. So the BST layer can improve the fatigue properties of the PZT-based capacitor. However, about 10% fatigue is still observed for all of the multilayered capacitors. We assume there are two possible reasons for it. One is due to the pinning of a few ferroelectric domains by point defects or space charge in the bulk of the PZT film. Since the thickness of BST is very small, the density of trap states in the bulk of PZT near the BST layer can be relatively

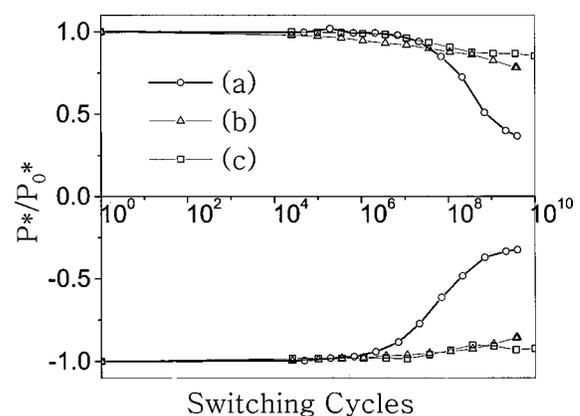


FIG. 3. The fatigue properties of PZT and BST/PZT/BST films. P^* is the switchable polarization of the films. P_0^* is the switchable polarization of first cycle. The measurement frequency is 2.5×10^4 Hz and the applied voltage is 9 V. Curve a: PZT film and 600 nm. Curve b: BST/PZT/BST, BST: 15 nm and PZT: 600 nm, and curve c: BST/PZT/BST, BST: 7.5 nm and PZT: 600 nm.

high. Another possible reason is that the dielectric constant of the BST layer decreases with the accumulation of oxygen vacancies or other point defects in it,⁷ which results in the decrease of the electric field applied on the PZT layer and thus the decrease of switchable polarization of the PZT layer.

In conclusion, the introduction of a BST layer between the PZT layer and the Pt electrode in PZT-based capacitors can greatly improve the fatigue properties of the PZT thin film. We attribute the effect of the BST layer to the absorption of oxygen vacancies or other point defects from the PZT layer. A multilayered capacitor with a very thin BST layer (thickness ~ 7.5 nm) has good polarization properties, such as high remnant polarization and rare fatigue properties after 10^{10} switching cycles.

- ¹O. Auciello, J. F. Scott, and R. Ramesh, *Phys. Today* **51**, 22 (1998).
- ²J. F. Scott and C. A. Araujo, *Science* (Washington, DC, U.S.) **246**, 1400 (1989).
- ³W. L. Warren, D. Dimos, B. A. Tuttle, R. D. Nasby, and G. E. Pike, *Appl. Phys. Lett.* **65**, 1018 (1994).
- ⁴E. L. Colla, D. V. Taylor, A. K. Tagantsev, and N. Setter, *Appl. Phys. Lett.* **72**, 2478 (1998).
- ⁵C. B. Eom, R. B. Van Dover, J. M. Phillips, D. J. Werder, J. H. Marshall, C. H. Chen, R. J. Cava, R. M. Fleming, and D. K. Fork, *Appl. Phys. Lett.* **63**, 2570 (1993).
- ⁶F. Yan, P. Bao, H. L. W. Chan, C. L. Choy, and Y. N. Wang, *Thin Solid Films* **406**, 282 (2002).
- ⁷F. Yan, P. Bao, X. B. Chen, J. S. Zhu, and Y. N. Wang, *Integr. Ferroelectr.* **33**, 379 (2001).
- ⁸J. J. Lee, C. L. Thio, and S. B. Desu, *J. Appl. Phys.* **78**, 5073 (1995).
- ⁹J. F. M. Cillessen, M. W. J. Prins, and R. M. Wolf, *J. Appl. Phys.* **81**, 2777 (1997).

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