

Enhanced fatigue-endurance of ferroelectric $\text{Pb}_{1-x}\text{Sr}_x(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ thin films prepared by sol-gel method

Y. Wang and Q. Y. Shao

Nanjing National Laboratory of Microstructure, Nanjing University, Nanjing 210093, China

J.-M. Liu^{a)}

Department of Applied Physics, Hong Kong Polytechnic University, Hong Kong, China, Nanjing National Laboratory of Microstructure, Nanjing University, Nanjing 210093, China, and International Center for Materials Physics, Chinese Academy of Sciences, Shenyang, China

(Received 30 June 2005; accepted 25 February 2006; published online 21 March 2006)

The polarization fatigue behaviors of ferroelectric $\text{Pb}_{1-x}\text{Sr}_x(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ (PSZT) thin films deposited on Pt-coated silicon wafers are investigated. Significantly enhanced fatigue endurance with increasing Sr doping and decreasing temperature is observed, and the almost fatigue-free performance up to 10^{10} switching cycles for PSZT ($x=0.2$) thin films at room temperature is identified. The dc-conductivity measurements suggest almost 20 times decreasing of the oxygen vacancy density as the Sr doping increases from $x=0$ to $x=0.2$. It is believed that the Sr-doping enhances the stability of oxygen ions and suppresses oxygen vacancies, consequently resulting in the improved fatigue endurance. © 2006 American Institute of Physics. [DOI: 10.1063/1.2188591]

Recently, ferroelectric thin films have been considerably investigated for the applications in integrated memory devices, especially ferroelectric random access memories (FeRAM).¹⁻³ Lead zirconate titanate, typically $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ (PZT), as one of the important candidate materials, however, shows a serious polarization fatigue (PF) effect, namely the vast degradation of polarization upon domain switching cycling. This PF effect thus greatly hinders practical utilization of PZT thin films.⁴⁻⁶ The physics underlying such a phenomenon may be essentially ascribed to oxygen vacancies (OVs) in PZT, although quite a few mechanisms other than the long-range migration and aggregation of OVs and domain pinning during the switching cycling have been proposed. Subsequently, Aurivillius layered perovskite oxide thin films, such as $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT), have drawn attention due to their excellent fatigue endurance.³ It is interesting to note that $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ with a crystal structure similar to SBT, still shows serious PF behavior.⁷ For SBT, it is believed that oxygen ions inside SrTa_2O_7 perovskite layers are more stable than those at Bi_2O_2 layers because of the strong Sr–O bonding,⁸ thus a low density of OVs in SBT was identified.⁹ The high oxygen stability associated with Sr–O bonding allows one to search for new candidate materials for FeRAM applications. One possibility is to dope Sr into PZT in order to enhance the stability of oxygen ions and devalue the mobility of OVs for long-range diffusion, while the good ferroelectric properties of PZT can be retained.

Earlier works on Sr-doped PZT, such as $\text{Pb}_{1-x}\text{Sr}_x(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ (PSZT), mainly concentrated on its microwave-band dielectric property for device orientations, such as phase shifter, variable frequency divider, and so on. Its ferroelectric performance has not yet received much attention.^{10,11} In this letter, we will study the ferroelectric PF behaviors of PSZT thin films based on the above argument on the Sr-doping effect. Although it was reported that Sr-doping at A sites will damage the ferroelectricity of PZT, and

in spite of the linear decreasing of the Curie temperature (T_c) with Sr-doping in $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$,¹¹ a low-level Sr doping is still allowed in order to improve the PF endurance without much damage to the room-temperature ferroelectricity because of the high Curie point and large polarization of PZT. We study the PF behaviors of PSZT thin films at $x=0-0.2$.

The PSZT thin films were deposited layer by layer on commercial Pt/TiO₂/SiO₂/Si substrates by sol-gel process and rapid thermal annealing (RTA). The detailed procedure of preparation was described elsewhere.¹¹ The postannealing was performed at 700 °C for 3 min in the flowing oxygen by RTA after adequate paralysis. The polycrystalline perovskite structures of the films with final thickness of ~400 nm were inspected by x-ray diffraction (XRD), as shown in Fig. 1. A number of Pt dots of 200 μm in diameter each were sputtered on the films as top electrodes. The dielectric constant as a function of temperature T was studied using a HP4294A impedance analyzer. The polarization-electric field (P - E) hysteresis loops and fatigue testing were carried out using a RT66A ferroelectric tester (Radiant Technologies Ltd., NM) with a pair of shield cables to connect the electrodes. The fatigue experiment was performed using a bipolar pulse, with a pulsed width of 8.6 μs and a period of 20 μs at a frequency of 50 kHz, and the nonvolatile component of the

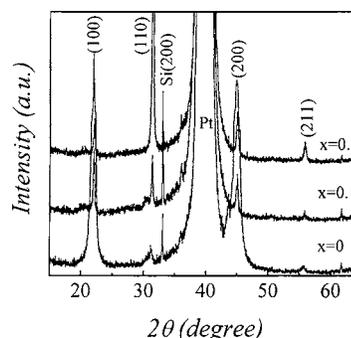


FIG. 1. XRD patterns of PSZT ($x=0, 0.1$, and 0.2) thin films on Pt-coated (100) silicon substrates.

^{a)} Author to whom correspondence should be addressed; electronic mail: liujm@nju.edu.cn

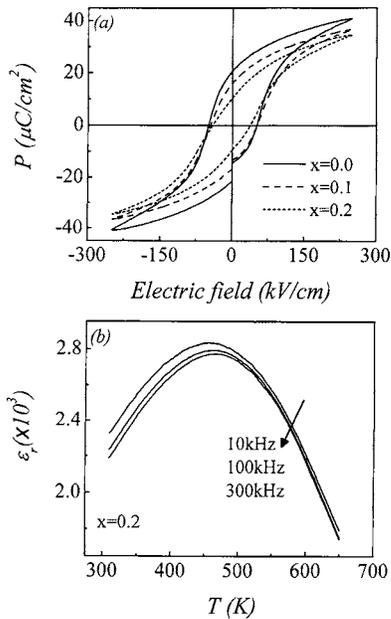


FIG. 2. (a) Room-temperature P - E hysteresis loops for PSZT ($x=0, 0.1,$ and 0.2) thin films. (b) Temperature dependence of dielectric constant ϵ_r for PSZT ($x=0.2$) thin films at three frequencies (10 kHz, 100 kHz, and 300 kHz).

switched polarization after N -switching cycles is $P_{NV} = P^* - P^\wedge$ or $P_{NV} = -P^* - (-P^\wedge)$, where P^* and P^\wedge refer to the pulsed charge. The low- T fatigue testing was performed by inserting the samples into a Janis closed-cycle refrigerator system (Janis Research Company, Inc.).

From Fig. 1, it is found that all prepared samples show a well-crystallized structure. No significant dependence of the lattice structure and parameters on Sr-content x is observed. The as-prepared PZT thin films slightly prefer the (100) orientation, but this preference disappears upon Sr doping and no more preferred orientation for PSZT ($x=0.2$) thin films is observed, noting that at $x=0.2$ the (110) reflection is compatible with the (100) reflection. Since PZT has its polarization along the $\langle 100 \rangle / \langle 001 \rangle$ orientation, the slightly decreased polarization of PSZT upon Sr doping, as confirmed below in Fig. 2, becomes obvious.

Figure 2(a) illustrates the P - E loops at room temperature for three PSZT thin films ($x=0.0, 0.1,$ and 0.2), respectively. Under the optimized conditions of sample preparation, the remnant and maximum polarizations under measurement, P_r and P_{\max} , reach up to $20 \mu\text{C}/\text{cm}^2$ and $40 \mu\text{C}/\text{cm}^2$, respectively for PZT, indicating good ferroelectric property of the films. With increasing x , P_r and P_{\max} decrease from 20 and 40 to $11 \mu\text{C}/\text{cm}^2$ and $34 \mu\text{C}/\text{cm}^2$, respectively. The coercive field E_c falls down slightly. This change may be ascribed to the change of the film orientation on one hand (as mentioned above), and the slight suppression of the Curie point on the other hand, due to the Sr doping. We measure the dielectric constant ϵ_r of PSZT ($x=0.2$) as a function of T at a voltage of 50 mV and different frequencies, as plotted in Fig. 2(b). Although the dielectric peak corresponding to the ferroelectric transitions for thin-film samples is much broader than that for single crystals and bulk ceramics, the Curie point for PSZT ($x=0.2$) thin films remains as high as $T_c \sim 455$ K, far above room temperature.

In spite of the weak x dependence of the film orientation, it seems that PZT-based thin films deposited on Pt-coated Si

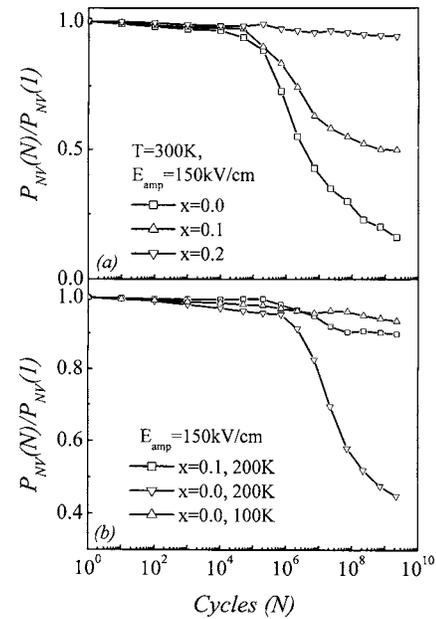


FIG. 3. Normalized P_{NV} plotted against switching cycle number N under $E_{\text{amp}}=150$ kV/cm for (a) PSZT ($x=0.0, 0.1, 0.2$) thin films at room temperature, and (b) PSZT ($x=0.1$) thin film at $T=200$ K, and PSZT ($x=0.0$) thin film at $T=200$ K and $T=100$ K.

substrates always show serious PF behaviors at room temperature, no matter the film orientation.^{4,5} In the other words, no significant orientation dependence of the PF behaviors has been reported so far. The fatigue endurance at room temperature for PSZT ($x=0.0, 0.1,$ and 0.2) thin films, respectively, is measured under $E_{\text{amp}}=150$ kV/cm, where E_{amp} is the magnitude of electric pulses for fatigue testing. The results are displayed in Fig. 3(a). As reported earlier, the fatigue of PZT is serious,^{4,12,13} but significantly improved fatigue resistance is observed upon the Sr doping. Referring to the data for PSZT ($x=0.2$) thin film, only a 6% reduction of nonvolatile polarization P_{NV} after more than 10^9 switching cycles is detected. Note here that the testing frequency for fatigue is 50 kHz, a low enough frequency for domain switching so that the dynamic effect associated with domain switching can be small. Therefore, the excellent PF resistance of Sr-doped PZT at an appropriate level $x=0.2$ is demonstrated.

Quite a few mechanisms responsible for the PF effect in ABO₃-type ferroelectric thin films, such as domain-wall pinning by the ion-type defects and trapped charges, prohibition of domain nucleation/switching, and formation of screening electric field, were proposed.¹³⁻¹⁸ It is basically believed that the formation of an interfacial layer between electrode and thin film due to the long-range diffusion of OV is of essential significance. Based on this concept, Dawber and Scott proposed a kinetic model (DS model) to interpret the PF effect associated with this long-range diffusion of OV, in which the fatigue is correlated with the density and activation barrier of OV. Although this model was once criticized,¹³ it is still applicable for cases of high-field limit, noting that the fatigue testing in the present experiment was undertaken under a high electric field. The DS model proposes the nonvolatile polarization $P(N)$ as a function of switching cycle number N :¹⁴

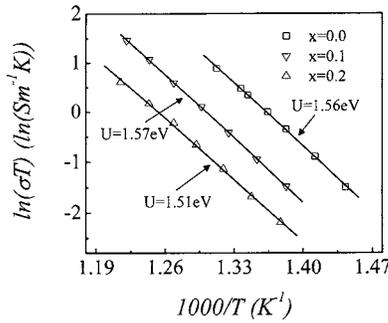


FIG. 4. dc-conductivity σ_{dc} of PSZT ($x=0, 0.1$, and 0.2) thin films plotted as a function of temperature T .

$$P(N) = A \exp \left[-6\lambda\mu\epsilon_s^{-1} e \exp \left(\frac{3a}{2} E_A \right) \frac{N}{f} \right] + B, \quad (1)$$

where λ is the density of thermally activated OVVs that may move into the interfacial layer under the cycling process, $\mu \sim \exp(-U/k_B T)$ is the mobility of OVVs with U the activation energy. The reader may refer to Ref. 14 for the definition of the other parameters. Given the values of T and E , the long-range diffusion of OVVs becomes essential in controlling the PF behaviors. Parameters λ and U upon the Sr doping are informative for understanding the physics of PF endurance, which can be evaluated by measuring the dc conductivity σ_{dc} satisfying the following equation:

$$\sigma_{dc} = \lambda q \mu = \frac{\lambda q D_0}{T} \exp(-U/kT), \quad (2)$$

where q is the carrier charge and D_0 is the pre-exponential of mobility μ . In Fig. 4, σ_{dc} is presented as a function of T for the three types of PSZT thin films ($x=0, 0.1$ and 0.2). The solid lines are the fitting results by Eq. (2). Clearly, σ_{dc} is lower as x is bigger over the whole T range. Although the dependence of σ_{dc} on x may not be uniquely ascribed to Eq. (2) and other mechanisms may contribute to σ_{dc} either, it is at least indirectly reflected that the reduction of oxygen vacancies is one main reason for the suppression of σ_{dc} , noting that the evaluated energy U is nearly independent of x . The evaluated density of OVVs for PSZT at $x=0.1$ and 0.2 is only 33.2% and 4.98% of that for PSZT at $x=0$ (PZT), respectively, assuming that D_0 is x independent. Therefore, the presented results indicate that the decreasing density of OVVs upon the Sr doping is the possible origin for the enhanced fatigue endurance of PSZT thin films.

In addition, the DS model predicts a tremendous T dependence of the PF behaviors, and better fatigue endurance is expected at lower T . The low- T fatigue testing for the PSZT thin films under $E_{amp} = 150$ kV/cm was performed and the data are presented in Fig. 3(b). The fatigue effect for PZT is largely suppressed as T decreases and the reduction of P_{NV} is only 6.6% after $N \sim 10^9$ at 100 K. The similar reduction of P_{NV} is observed for PSZT ($x=0.1$) at 200 K and PSZT ($x=0.2$) at room temperature. While the temperature effect is essentially associated with the suppression of the mobility of OVVs at low T , the Sr doping lowers the density of OVVs in the samples.

The physics underlying the effect of Sr doping in PZT can also be understood by consulting to earlier studies on layered Aurivillius ferroelectric oxides. As mentioned above, SBT is fatigue free at room temperature. However,

$\text{Bi}_3\text{TiTaO}_9$ with Sr ions replaced by Bi ions and a half of Ta ions substituted by Ti ions shows serious fatigue failure.¹⁹ This manifests that the oxygen ions near Bi ions are less stable than those near Sr ions, as shown by x-ray photoelectron spectroscopy study.⁸ Furthermore, the La doping into $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ prohibits the volatility of Bi ions and enhances the stability of Ti-O octahedron,²⁰ and thus suppresses the mobility of OVVs. We argue that Pb ions in PZT, like Bi ions in SBT, may destabilize the oxygen ions, allowing generation and long-range diffusion of OVVs in PZT thin films although Pb benefits essentially to the ferroelectricity. The Sr substitution of Pb efficiently intensifies the chemical stability of perovskite structure, and hinders the generation of OVVs. Consequently, the suppression of the long-range diffusion of OVVs toward the film/electrode interface layer is responsible for the improved fatigue endurance in PSZT thin films.

In summary, we have investigated the ferroelectric fatigue behaviors of PSZT ($x=0.0, 0.1$, and 0.2) thin films prepared by sol-gel technique. It has been revealed that the Sr-doping improves significantly the fatigue endurance of the thin films but the ferroelectric property remains roughly undamaged. The fatigue-free performance up to 10^{10} switching cycles for PSZT ($x=0.2$) thin films at room temperature has been demonstrated. The dc-conductivity measurements suggest that the density of OVVs in PSZT ($x=0.1$ and 0.2) is only 33.2% and 4.98% of that in PZT. It is argued that the low density of OVVs in PSZT thin films is responsible for the improved fatigue endurance.

This work was supported by the National Nature Science Foundation of China (Grant nos. 10474039, 50332020, and 10021001), the National Key Projects for Basic Research of China (2002CB613303). One of the authors (J. M. L.) would like to thank the Hong Kong Polytechnic University for supporting this work through Project B-Q552.

¹J. F. Scott and C. A. Araujo, *Science* **246**, 1400 (1989).

²O. Auciello, J. F. Scott, and R. Ramesh, *Phys. Today* **51**, 22 (1998).

³C. A. P. de Araujo, J. D. Cuchiare, L. D. McMillan, M. C. Scott, and J. F. Scott, *Nature (London)* **374**, 627 (1995).

⁴E. L. Colla, D. V. Taylor, A. K. Tagantsev, and N. Setter, *Appl. Phys. Lett.* **72**, 2478 (1998).

⁵L. F. Schloss, P. C. McIntyre, B. C. Hendrix, S. M. Bilodeau, J. F. Roeder, and S. R. Gilbert, *Appl. Phys. Lett.* **81**, 3218 (2002).

⁶A. Q. Jiang, J. F. Scott, M. Dawber, and C. Wang, *J. Appl. Phys.* **92**, 6756 (2002).

⁷P. C. Joshi and S. B. Krupanidhib, *J. Appl. Phys.* **72**, 5827 (1992).

⁸B. H. Park, S. J. Hyun, S. D. Bu, T. W. Noh, J. Lee, H.-D. Kim, T. H. Kim, and W. Jo, *Appl. Phys. Lett.* **74**, 1907 (1999).

⁹D. Wu, A. D. Li, and N. B. Ming, *Appl. Phys. Lett.* **84**, 4505 (2004).

¹⁰M. Jain, N. K. Karan, R. S. Katiyar, A. S. Bhalla, F. A. Miranda, and F. W. Van Keuls, *Appl. Phys. Lett.* **85**, 275 (2004).

¹¹K. T. Kim and C. I. Kim, *Thin Solid Films* **420**, 544 (2002).

¹²J. F. Scott, *Ferroelectrics Memories* (Springer, Heidelberg, 2000), pp. 132–142.

¹³A. K. Tagantsev, I. Stolichnov, E. L. Colla, and N. Setter, *J. Appl. Phys.* **90**, 1387 (2001).

¹⁴M. Dawber and J. F. Scott, *Appl. Phys. Lett.* **76**, 1060 (2000).

¹⁵J. F. Scott and M. Dawber, *Appl. Phys. Lett.* **76**, 3801 (2000).

¹⁶W. L. Warren, D. Dimos, B. A. Tuttle, R. D. Nasby, and G. E. Pike, *Appl. Phys. Lett.* **65**, 1018 (1994).

¹⁷J. Lee, S. Esayan, A. Safari, and R. Ramesh, *Appl. Phys. Lett.* **65**, 254 (1994).

¹⁸A. K. Tagantsev, M. Landivar, E. Colla, and N. Setter, *J. Appl. Phys.* **78**, 2623 (1995).

¹⁹B. S. Kang, B. H. Park, S. D. Bu, S. H. Kang, and T. W. Noh, *Appl. Phys. Lett.* **75**, 2644 (1999).

²⁰B. H. Park, B. S. Kang, S. D. Bu, T. W. Noh, J. Lee, and W. Jo, *Nature (London)* **401**, 682 (1999).