Low-temperature switching fatigue behavior of ferroelectric $SrBi_2Ta_2O_9$ thin films

G. L. Yuan, J.-M. Liu,[a] S. T. Zhang, D. Wu, Y. P. Wang, and Z. G. Liu
Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China and International Center for Materials Physics, Chinese Academy of Sciences, Shenyang, China

H. L. W. Chan and C. L. Choy
Department of Applied Physics, Hong Kong Polytechnic University, Kowloon, Hong Kong and Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China

(Received 18 July 2003; accepted 25 November 2003)

The ferroelectric hysteresis and fatigue behavior over a wide temperature range from 290 to 50 K for $SrBi_2Ta_2O_9$ thin films with Pt electrodes on silicon substrates, prepared by metalorganic decomposition (MOD) and pulsed-laser deposition (PLD), are investigated. It is found that given a fixed electrical field amplitude, the coercivity of all films increases with decreasing temperature T. The saturated hysteresis loop easily obtained for the MOD-prepared thin films has its remnant polarization enhanced with decreasing T, but the PLD-prepared samples exhibit minor loops whose remnant polarization decays with decreasing T. While the films prepared by MOD exhibit improved fatigue resistance at low T, significant fatigue effect at low T is observed for the films prepared by PLD. Although we cannot rule out the effect of strain, the experimental results can be explained by competition between pinning and depinning of domain walls, which are dependent of temperature and defect charges. [DOI: 10.1063/1.1644056]

Recently, the use of ferroelectric materials for nonvolatile memory devices, in particular, ferroelectric random access memories (FRAMs), has attracted much interest. For ferroelectric memory applications, high remnant polarization, high dielectric permittivity, low operation voltage, and low leakage current are necessary. In spite of intensive studies in past decades, the low-temperature performance of ferroelectric thin films has not been understood as well as the room-temperature one.[1,2] Nevertheless, the temperature dependence of ferroelectric properties is one of the interesting issues, in view of not only technological applications, but also in a fundamental sense.[3] In fact, FRAM devices may undergo service at a low-temperature circumstance, such as in space. In addition, the temperature dependence is helpful for us to understand the polarization degradation mechanism; that is, the switching fatigue mechanism. It was reported that $SrBi_2Ta_2O_9$ (SBT) thin films deposited on Si wafers by pulsed-laser deposition (PLD) show a worse fatigue-resistance property when temperature T decreases. The measured remnant polarization P_r becomes smaller upon decreasing T from 300 to 100 K.[4] Therefore, it would be interesting to investigate whether this observed effect shows any general significance or relies on the materials and technique of thin-film fabrication. In this letter, we study the temperature dependence of the ferroelectric property of SBT thin films prepared by metalorganic decomposition (MOD) and PLD for a comparison study.

The SBT thin films were deposited on commercially available $Pt/TiO_2/SiO_2/Si$ substrates with Pt dots of 0.2 mm diameters deposited onto the top surface as top electrodes. All the procedures of preparation were optimized in terms of enhanced crystallinity and electrical property, and details of the preparation description were reported elsewhere.[5,6] In short, the SBT thin films were prepared by MOD and PLD, respectively. The post-annealing on MOD samples (SBT-MOD) was done in an oxygen-filled rapid-thermal-annealing furnace at 650 °C layer-by-layer, while the PLD samples (SBT-PLD) were post-annealed in flowing oxygen ambient at 650 °C. All SBT samples with preferred (115) orientation were checked by x-ray diffraction for microstructure characterization. The thicknesses of SBT-MOD and SBT-PLD films, which are measured by scanning electron microscopy (SEM), are 660 and 377 nm, respectively. The grain sizes checked by SEM are ~60 and 80 nm for SBT-MOD and SBT-PLD films, respectively. The electrical properties, including leakage current, ferroelectric hysteresis, and switching-fatigue behaviors for all the samples, were performed in a temperature-controllable vacuum chamber (20 Pa), in which the samples were packaged. Temperature T ranges from 290 to 50 K in the present experiment. A pair of shielded cables was used to connect the Pt electrodes and RT66A standard ferroelectric tester (Radiant Technologies Ltd., NM). The fatigue experiment was performed using a bipolar pulse, with a pulsed width of 8.6 μs and period of 20 μs. The nonvolatile component of the switched polarization is $P_{nv}=P^*-P^\wedge$ or $P_{-nv}=P^*-(-P^\wedge)$, where P^* and $P^\wedge$ refer to the pulsed-charge measurement by RT66A tester.

We first look at the T dependence of SBT-MOD thin films. Figure 1(a) presents the hysteresis loops. As T is lowered from 290 to 105 K, the loops are well saturated under a voltage V with amplitude $V_{max}=19$ V. The saturated polarization P_s at $V=\pm V_{max}$ changes little, while the coercive voltage V_c and P_r increase with decreasing T. At $V_{max}=7$ V, no saturated loop is obtainable at 105 K and both P_s and P_r decrease with decreasing T. For SBT-PLD thin films, the hysteresis loops cannot saturate even at $V_{max}=15$ V, and both P_r and P_s decrease as T decreases from 290 to 105 K, as

[a]Author to whom correspondence should be addressed; electronic mail: liujm@nju.edu.cn

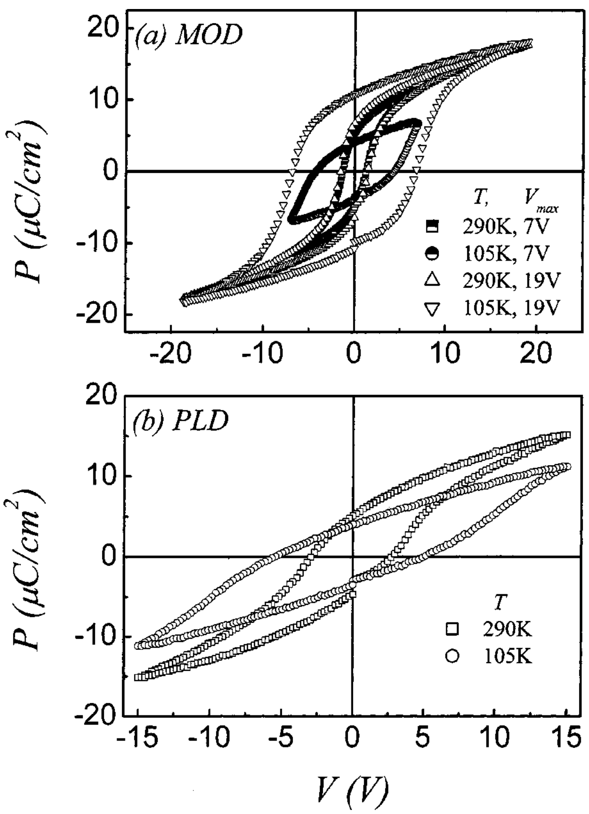

FIG. 1. Measured polarization–voltage ($P-V$) loops for (a) SBT-MOD thin films prepared by MOD and (b) SBT-PLD thin films deposited by PLD.

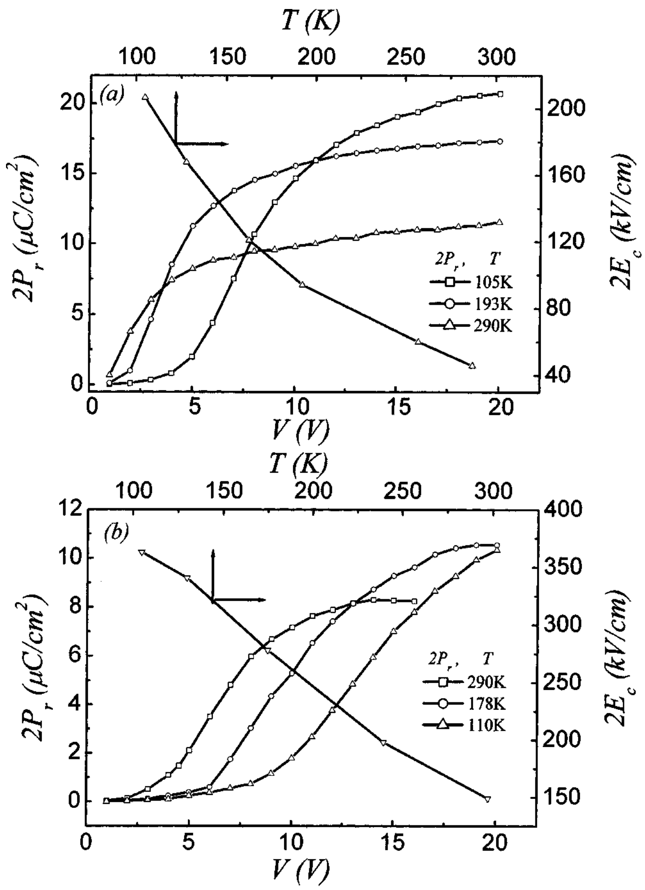

FIG. 2. Left axis and bottom axis: Parameter $2P_r$ plotted against voltage amplitude $V_{\max}$ at various T. Right axis and top axis: Parameter $2E_c$ as a function of T under $V_{\max}=20$ V for (a) SBT-MOD and (b) SBT-PLD thin films.

shown in Fig. 1(b), indicating that the domain switching is not complete at low T. To understand these effects, we plot $2V_c$ against T and $2P_r$ as a function of $V_{\max}$ at various T for SBT-MOD thin films, in Fig. 2(a). As T increases from 105 to 290 K, $2V_c$ drops rapidly from 13.6 to 3 V, while P_r reaches its saturated value as $V\sim6$, ~10, and ~18 V at $T=290$, 193, and 105 K, respectively. While P_s remains nearly unchanged, an enhanced P_r with decreasing T indicates less loss of polarization when V recovers to zero from $\pm V_{\max}$. Since the negative effect of thermal fluctuations is weaker and V_c is higher at lower T, fewer domains switch back to the original polarization state (or backswitching) after the voltage turns off. Thus, the gap of the loop along the P axis ($P_r^{\wedge}$) is smaller at a lower T, suggesting the less loss of polarization during the retention.[7,8]

For SBT-PLD thin films, as shown in Fig. 2(b), although the loops are saturated and P_r does not change much as $V_{\max}>10$ and >16 V at $T=290$ and 178 K, respectively, the hysteresis loop at 105 K is still minor (not well saturated) even at $V=V_{\max}\sim20$ V. For the minor loop, both P_s and P_r decrease with decreasing T, due to the fact that the pinning of domains is more serious and the domain switching becomes less complete at lower T. In fact, similar observations were reported earlier,[4] although our results show some quantitative differences.

The switching fatigue behaviors of SBT-MOD samples at different T are shown in Fig. 3(a). At 290 K, both P_{nv} and $P_{-\mathrm{nv}}$ first increase and then decrease with switching cycle number N. After $N\sim10^{10}$, they show an approximate 8% increase and 15% reduction under $V_{\mathrm{amp}}=10$ and 5 V, respectively, where V_{amp} is the amplitude of the voltage pulses for fatigue test. Since $V_{\mathrm{amp}}=5$ V is close to V_c at 290 K, a high density of domain walls is expected, which easily leads to the switching fatigue.[9,10] However, at $T=105$ K, P_{nv} and $P_{-\mathrm{nv}}$ show only 2% and 6.6% reduction at $V_{\mathrm{amp}}=18$ and 10 V, respectively. Although $V_{\mathrm{amp}}=10$ V is not much higher than V_c, the measured P_{nv} is 4.6% lower than P_{nv} measured at $V_{\mathrm{amp}}=18$ V. This 4.6% reduction can be roughly viewed as the contribution of the pinned domain walls which cannot be depinned under $V_{\mathrm{amp}}=10$ V. Therefore, the polarization degradation at 290 K after $N\sim10^{10}$ is more remarkable than that at 105 K. In order to understand the fatigue mechanism of SBT at low T, the fatigue behaviors of SBT-PLD were also measured, as shown in Fig. 3(b). One finds that the fatigue-resistance property is excellent at 290 K, but unfortunately, a polarization decay of $\sim34\%$ after $N\sim10^{10}$ was recorded at 105 K. At room temperature, SBT-MOD and SBT-PLD films show two stages of switching charge change during cycling: rejuvenation (wake up) and fatigue. Here, it should be pointed out that the two stages can be explained in terms of the formation of spatially inhomogeneous internal bias field during cycling (kinetic imprint effect).[11,12] As shown in Fig. 3, the rejuvenation stage disappears below 150 K for both SBT-MOD and SBT-PLD films.

One of the popular mechanisms for Aurivillius-based SBT is that an aggregation of charges at domain walls can lock the domain from switching.[9,13–15] In addition, the possible reasons responsible for the switching fatigue include the prohibition of switching/nucleation at the electrode/film

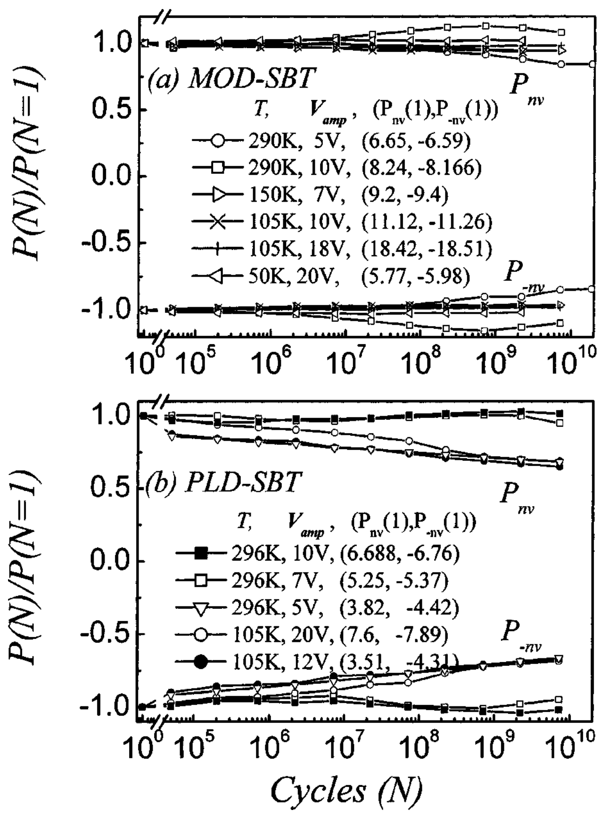

FIG. 3. Normalized nonvolatile polarization P_{nv} and $P_{-\mathrm{nv}}$ plotted against number of switching cycles N for (a) SBT-MOD thin films and (b) SBT-PLD thin films. $P_{\mathrm{nv}}(1)$ and $P_{-\mathrm{nv}}(1)$ are data measured after the first switching cycle.

interface, formation of the 90° domains and resultant strain, and formation of the planar defects parallel to the film surface formed by electromigration.[15] In the case of domain wall pinning, the defect charges trap at the internal domain boundaries. Therefore, all of these mechanisms, except the 90° domains, take into account of the effect of defects and trapped charges. For SBT-PLD films, the hysteresis loops are tilted at 105 K after $N \sim 10^{10}$ bipolar cycle switches with $V_{\mathrm{amp}} = 12$ V, these tilted loops can be rejuvenated well by domain switching at a much higher field $V_{\max} = 18$ V. Therefore, the fatigue behaviors at low T may be controlled by a competition between the domain wall pinning and depinning as it does at RT.[13] As T is lowered, the domain wall pinning becomes harder because the ionic mobility (diffusion) and leakage current are exponentially reduced with decreasing T.[15–18] However, note that the depinning of the frozen domains is also more difficult because fewer and fewer defects and trapped charges can be activated when T is low. The two mechanisms give rise to the opposite effects, and the low-T fatigue behaviors are essentially determined by the competition of the two. As mentioned earlier, the disappearance of the rejuvenation stage below 150 K demonstrates that the depinning is more difficult at lower T.

The mechanisms just described are adopted to explain our experimental data of SBT-MOD, whose fatigue resistance at low T is excellent irrespective of V_{amp}. The density of the pinned domain walls depends on the density of defect charges, density of domain walls (related to V_{amp}), and T, while the depinned domain walls depends only on the density of the pinned domain walls and T. At low T, the pinning of domain walls becomes difficult; thus, the density of pinned domain walls becomes low, which is one factor to suppress the density of depinned domain walls. The density of both pinned and depinned domain walls is low at low T. They do not effectively change P_{nv} and $P_{-\mathrm{nv}}$ as they do at RT. Thus, P_{nv} and $P_{-\mathrm{nv}}$ stay roughly constant below 105 K after $N \sim 10^{10}$. For SBT-PLD, with decreasing T, the density of defect charges may be still high enough to easily pin domain walls, while the density of depinned domain walls becomes much lower, due mainly to the temperature effect. A big difference between the densities of the pinned walls and depinned walls at low T contributes to the serious fatigue effect observed at low T.

Besides the big difference in coercive field E_c between SBT-MOD and SBT-PLD samples, the difference in the fatigue behaviors between the two types of samples suggests that the density of defect charges in SBT-MOD is lower than that of SBT-PLD. In preparing SBT-PLD sample, the impact of high-speed particles during the deposition and serious ionization process of laser ablation may generate large strains and a high density of defect charges. Here, we cannot rule out the effect of strain. In fact, because of the different thermal expansion coefficients of the film and substrate, the built-in strains in the films deposited by PLD will be enlarged with decreasing temperature.[19]

The authors acknowledge the support from the Natural Science Foundation of China (project 50332020), the National 973 Project of China (2002CB613303).

[1] C. J. Brennan, R. D. Parrella, and D. E. Larsen, Ferroelectrics **151**, 33 (1994).
[2] E. Paton, M. Brazter, S. Mansour, and A. Bement, Integr. Ferroelectr. **18**, 29 (1997).
[3] T. Mihara, H. Watanabe, and C. A. Araujo, Jpn. J. Appl. Phys., Part 1 **33**, 3996 (1994).
[4] P. X. Yang, D. L. Carroll, J. Ballato, and R. W. Schwartz, Appl. Phys. Lett. **81**, 4583 (2002).
[5] D. Wu, A. D. Li, H. Q. Ling, T. Yu, Z. G. Liu, and N. B. Ming, Appl. Phys. A: Mater. Sci. Process. **71**, 597 (2000).
[6] Y. P. Wang, T. Zhu, and Z. G. Liu, Appl. Phys. A: Mater. Sci. Process. **74**, 665 (2002).
[7] K. W. Lee and W. J. Lee, Jpn. J. Appl. Phys., Part 1 **41**, 6718 (2002).
[8] D. J. Taylor, P. K. Larsen, G. J. M. Dormana, and A. E. M. De Veirman, Integr. Ferroelectr. **7**, 123 (1995).
[9] A. K. Tagantsev, I. Stolichnov, E. L. Colla, and N. Setter, J. Appl. Phys. **90**, 1387 (2001).
[10] H. A. Al-Shareef, D. Dimos, T. J. Boyle, W. L. Warren, and B. A. Tuttle, Appl. Phys. Lett. **68**, 690 (1996).
[11] V. Ya. Shur, E. L. Rumyantsev, E. V. Nikolaeva, E. I. Shishkin, and I. S. Baturin, J. Appl. Phys. **90**, 6312 (2001).
[12] A. Gruverman, B. J. Rodriguez, A. I. Kingon, R. J. Nemanich, J. S. Cross, and M. Tsukada, Appl. Phys. Lett. **82**, 3071 (2003).
[13] D. Dimos, H. A. Al-Shareef, W. L. Warren, and B. A. Tuttle, J. Appl. Phys. **80**, 1682 (1996).
[14] I. Stolichnov, A. Tagantsev, N. Setter, J. S. Cross, and M. Tsukada, Appl. Phys. Lett. **74**, 3552 (1999).
[15] J. F. Scott and M. Dawber, Appl. Phys. Lett. **76**, 3801 (2000).
[16] S. Zafar, E. J. Robert, J. Bo, W. Bruce, C. Peir, D. Taylor, and G. Sherry, Appl. Phys. Lett. **73**, 175 (1998).
[17] S. Bhattacharyya, A. Laha, and S. B. Krupanidhi, Appl. Phys. Lett. **91**, 4543 (2002).
[18] *Ferroelectrics Memories*, edited by J. F. Scott (Springer, Heidelberg, 2000), pp. 132–142.
[19] J. V. Mantese, N. W. Schubring, A. L. Micheli, M. P. Thompson, R. Naik, G. W. Auner, I. B. Misirlioglu, and S. P. Alpay, Appl. Phys. Lett. **81**, 1068 (2002).