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High-resolution electron microscopy investigations on stacking faults in $SrBi_2Ta_2O_9$ ferroelectric thin films

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Structural planar defects in the $SrBi_2Ta_2O_9$ (SBT) films with 10 mol % excess Bi grown in $Pt/TiO_2/SiO_2/Si$ substrates by metalorganic deposition have been observed by high-resolution electron microscopy. It was found that these stacking defects were planar defects with extra Bi–O planes normal to the *c* axis. These structural defects are expected to effectively improve the ferroelectric response and fatigue-resistance characteristics of SBT films because of the extra Bi–O planes having higher strucutral flexibility and alleviating the mechanical stresses and strains as well as injected-charge problems. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1332106]

Ferroelectric thin films have received considerable attention for nonvolatile memory applications because of their low operating voltage, high switching speed, and better endurance.[1–3] In the past decade, ferroelectric films of the $Pb(Zr_xTi_{1-x})O_3$ (PZT) family are the most popular materials for nonvolatile memory applications. However, PZT thin films with Pt electrodes exhibit significant polarization fatigue during the electrical field cycling, although this problem has been mostly alleviated by using oxide electrodes such as $YBa_2Cu_3O_7$,[4] $La_{1-x}Sr_xCoO_3$,[5] RuO_2,[6] and IrO_2.[7] An alternative approach to control the fatigue problem in ferroelectric capacitors is to use other ferroelectric materials. Recently, issues with fatigue and concerns of environment, safety, and health have prompted interest in the bismuth layered perovskite materials such as $SrBi_2Ta_2O_9$ (SBT). It has been demonstrated that Pt/SBT/Pt capacitors exhibit practically no polarization fatigue up to about 10^{12} switching cycles, good retention characteristics, and low leakage currents.[8] The absence of fatigue in SBT is thought to be the fact that electronic traps in this material are shallow, which results in weak pinning of domain walls. Therefore, the domain walls are easily depinned by an external field.[9,10] Thus, factors that can influence the electronic trap states in SBT such as impurities and strucutral defects, are critically important to the properties of this material. The physical properties of SBT thin films have been extensively investigated with an emphasis on nonvolatile memory applications, however, up to date the basic structure, intrinsic properties, and effects of microstructural defects on physical properties of SBT films are not well understood mainly because of the lack of well-characterized strucutral defects at the atomic-scale. High-resolution transmission electron microscopy (HRTEM), which can image the strucutral defects at the atomic scale and determine the microstructures with atomic-level accuracy, is proved to be invaluable in characterizing structural defects. In this letter, we report the direct HRTEM observations on stacking faults with extra Bi–O planes normal to the *c* axis in SBT ferroelectric films prepared by metalorganic deposition (MOD). The relationship between strucutral defects and ferroelectric properties is also discussed.

SBT thin films with 10 mol % excess bismuth were deposited on $Pt/TiO_2/SiO_2/Si$ substrates at 750 °C by MOD, details were described elsewhere.[11] For electrical measurements, Pt top electrodes were sputter deposited onto the SBT films through a shadow mask with an area of 3.14×10^4 cm^2. The ferroelectric properties of SBT films were measured by RT6000HVS tester (Radiant Technologies, Inc.). The plan-view samples suitable for HRTEM observations were prepared by a combination of mechanical thinning, dimpling, and ion milling. The samples were cut and ground on substrate side to a thickness of ~30 μm. The samples were then dimpled on the substrate side to approximately 15 μm at the center, and ion milled with 4 kV argon ion at incident angle of from 15° to 12°. After perforation, the samples were further milled with 1.5 kV ions with an incident angle of 10° to remove surface damage and contamination. The microstructural defects of SBT films were observed by HRTEM (JEOL, JEM-4000EX) operated at 400 kV with point-to-point resolution of 0.19 nm.

SBT material is one member of family of multilayered Aurivillius compounds.[12] Its structure consists of one Sr–Ta–O perovskite block situated between two Bi_2O_2 layers, as shown in Fig. 1(a). The Sr^{2+} is surrounded by 12 oxygen ions as in perovskite and is essentially passive. The Ta^{5+} is octahedrally coordinated by six oxygen ions. At three of the four distinct oxygen sites, O(1) and O(4), O(5) are bonded to two Ta ions, as in perovskite, while O(2) is apically bonded to one Ta, as shown in Fig. 1(b). Bi and O(3) form a rippled Bi_2O_2 layer, in which Bi ions lie alternatively above and below the O(3) plane, as in the Pb–O layer in tetragonal PbO. The Bi sites are asymmetric, forming four short bonds to O(3) sites and four longer bonds to O(2) sites. The crystal structure of SBT material has been refined by electron and neutron diffraction techniques ($a=0.55306$ nm, $b=0.55344$ nm, $c=2.49839$ nm), and orthorhombic distortion with space group $A2_1am$ has been revealed.[13] With the $A2_1am$ orthorhombic symmetry, the *a* axis is the polar axis. Atomic displacements along the *a* axis from the correspond-

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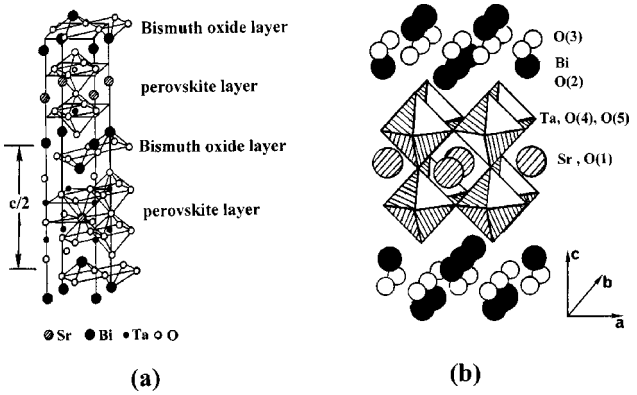

FIG. 1. (a) Crystal structure of $SrBi_2Ta_2O_9$, (b) perspective drawing of undistorted $SrBi_2Ta_2O_9$ from $c/4$ to $3c/4$.

ing positions in the parent tetragonal (I4/mmm) structure cause ferroelectric spontaneous polarization. Displacement along the *b* and *c* axes, in contrast, are cancelled due to the presence of glide and mirror planes, respectively, thus, they do not contribute the total polarization.[14]

Our previous measurements on ferroelectric properties of SBT films as a function of the amount of excess bismuth indicate that the polarization-electric field (*P–E*) hysteresis loop of the SBT film with 10 mol % excess Bi is the best, as shown in Fig. 2. The related fatigue characteristic is illustrated in Fig. 3. The good ferroelectric properties of the SBT films with 10 mol % excess Bi are closely correlated to its microstructures, particularly the structural defects revealed by HRTEM. Figure 4 shows a plane-view HRTEM image of the SBT film with 10 mol % excess Bi deposited on $Pt/TiO_2/SiO_2/Si$ substrate. The film is viewed along the [110]-zone axis direction. The modulated structures of the perovskite layers and bismuth oxide layers along the *c* axis in SBT film are obviously observed. The *c*-axis lattice fringes are clearly resolved. The periodic fringes with a spacing of 1.25 nm correspond to Bi_2O_2 layers. The lattice parameter of the *c* axis is measured to be 2.50 nm, which is in good agreement with the structural data refined by x ray and

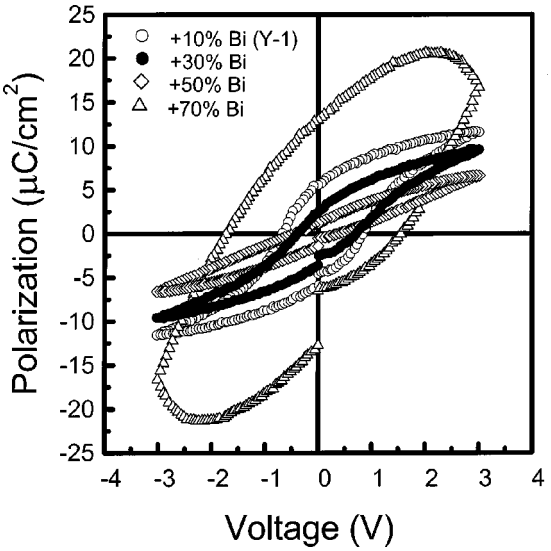

FIG. 2. *P–E* hysteresis loops of the SBT films with different amount of excess bismuth, in which the *P–E* loop of SBT film with 10 mol % excess bismuth is the best.

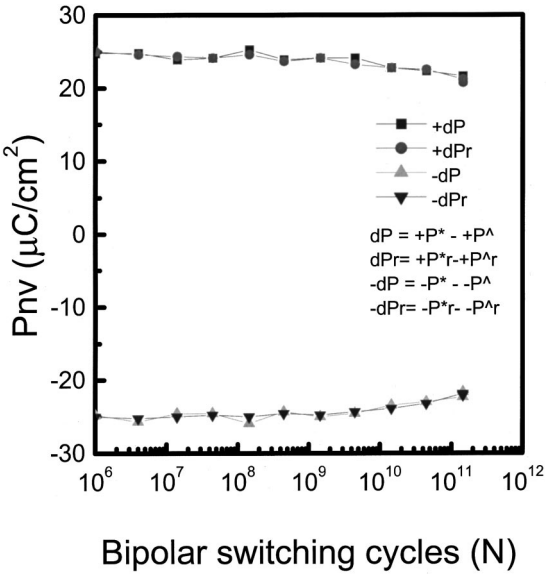

FIG. 3. Fatigue characteristics of the SBT film with 10 mol % excess bismuth.

neutron powder diffraction.[13–15] From the observed image contrast, stacking defects are observed, which show significantly dark background, as marked by symbols >-< in Fig. 4. According to the strucutral data determined by x ray and neutron diffraction, and the distance between the cationic planes, the stacking faults are considered to be extra Bi–O planes, which are resulted from excess bismuth in the SBT films. In general, repetition distances of two, three, four, or more perovskite ABO_3 (A is divalent metal ion and B is pentavalent metal ion) blocks can be obtained between bismuth planes in the Bi-layered Aurivillius compound, this can

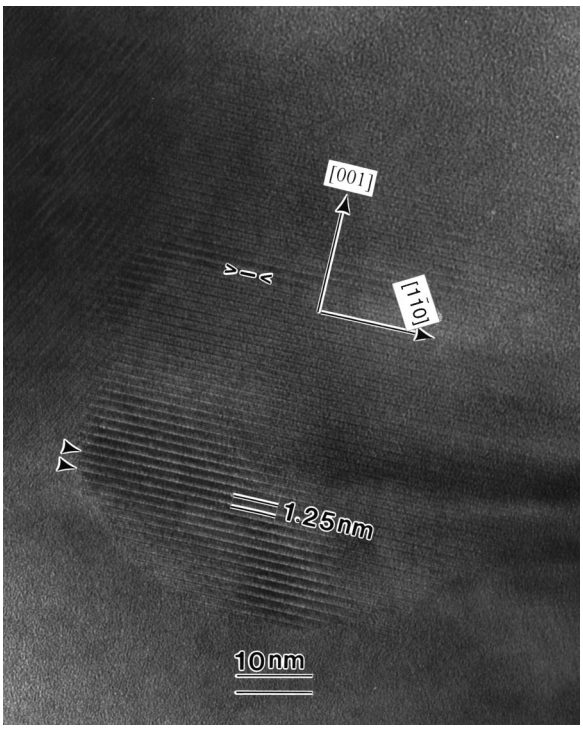

FIG. 4. [110]-zone axis HRTEM image of the modulated structures of the perovskite layers and bismuth oxide layers along the *c* axis in the SBT film with 10 mol % excess bismuth. The main distinguishing feature consists of planar stacking defects with extra Bi–O planes normal to the *c* axis.

produce crystals of perfect translational symmetry and also incommensurate (modulated) strucutres. Since the bismuth oxide planes have a net electrical charge, their positioning in the lattice is self-regulated to compensate for space charge near electrodes. Furthermore, bismuth oxide planes can well minimize interlayer stress in layered compounds such as high-T_c superconductors because intergrowth superlattice compounds have a unique ability to convert point defects into strain lattice planes.[16] In this case, point defects are less likely to pin domains and degrade switched charge. Therefore, the existence of bismuth oxide planes in SBT films is critically important to the ferroelectric properties. Theoretical calculations of both valence band maximum and the conduction band minimum in SBT have shown that the Bi displacement could make the largest contribution to the ferroelectricity of SBT because the Bi displacement is substantial due to the weaker bonding of the Bi–O layer.[9] The electronic response of SBT is dominated by the Bi–O layers. Quantitative contributions of the constituent ions in SBT to the total spontaneous ferroelectric polarization can be calculated by $P_s=\Sigma(m_i\Delta x_i q_i)/V$, where m_i is the site multiplicity, Δx_i is the atomic displacement along the a axis from the corresponding position in the orthorhombic structure, q_i is the ionic charge for the ith constituent ion, and V is the volume of the unit cell. The calculated results also indicate that the atomic displacement of Bi in the Bi–O layers play an important role in the large ferroelectric spontaneous polarization of SBT. The existence of extra Bi–O layers at the stacking faults will therefore enhance the contribution of Bi^{3+} ion to the ferroelectric polarization of SBT and affect the electronic response of SBT, although the overall effect should be relatively small because of the low volume fraction within the film. Compared with the normal sequence of Bi–O layers along the c axis, the extra Bi–O layers should have much higher strucutral flexibility because of weaker bonding in the extra Bi–O layers. Therefore, they can release the interlayer stress effectively and compensate for the space charges, which are thought to be the main causes of the fatigue in ferroelectrics.[8] Thus, the fatigue-resistance characteristics of SBT films are expected to be improved considerably by the existence of the stacking faults with extra Bi–O layers.

In summary, the modulated structures of the perovskite layers and bismuth oxide layers along the c axis in the SBT film with 10 mol % excess Bi have been resolved by HRTEM. Strucutral stacking faults are observed as planar defects with extra Bi–O planes normal to the c axis. The existence of such stacking faults is beneficial to improving the fatigue-resistance characteristics of the SBT films because the extra Bi–O planes have higher structural flexibility and can effectively alleviate the mechanical stresses and strains as well as injected-charge problems.

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