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Electrical properties of $Sr_3Bi_4Ti_6O_{21}$ thin films

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ABSTRACT Highly *c*-axis-oriented $Sr_3Bi_4Ti_6O_{21}$ (SBTi) thin films were fabricated on Pt-coated Si substrates by pulsed laser deposition (PLD). The structures were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM) and scanning electron microscopy (SEM). No peaks of $SrTiO_3$ (STO) could be detected in the XRD pattern, indicating the existence of the SBTi single phase. Good ferroelectric hysteresis loops of the films with Pt electrodes were obtained. With an applied field of 400 kV/cm, the measured remanent polarization (P_r) and coercive field (E_c) values were 4.1 $\mu C/cm^2$ and 75 kV/cm respectively. The films showed little fatigue after 2.22×10^9 switching cycles: the nonvolatile polarizations decreased by less than 5% of the initial values. The dielectric constant and the loss tangent of the films were measured to be 363 and 0.04 at 100 kHz. These results might be advantageous for nonvolatile ferroelectric random access memory (NVFRAM) and dynamic random access memory (DRAM).

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In recent years, ferroelectric thin films of Bi-layered oxide (Aurivillius phases) have been widely studied for use in nonvolatile ferroelectric random access memory (NVFRAM) due to their low coercive field and leakage current, long retention, minimal tendency to imprint and little fatigue with the usual platinum electrode [1]. The Bi-layered oxide family can be described as $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$, where A represents Bi, Ba, Pb, Sr, Ca, K, Na and rare-earth elements, B represents Ti, Ta, Nb, W, Mo, Fe, etc. and m represents the number of BO_6 octahedra between two neighboring Bi_2O_2 layers. For example, $SrBi_2Ta_2O_9$ ($m = 2$), $Bi_4Ti_3O_{12}$ ($m = 3$), $SrBi_4Ti_4O_{15}$ ($m = 4$) and $Sr_2Bi_4Ti_5O_{18}$ ($m = 5$) have two, three, four and five octahedra respectively. Obviously, the Bi-layered oxide family provides a possibility to optimize the ferroelectric properties by alternating the elements of both A and B, and naturally manipulating the layered structure with the number of the BO_6 octahedra and, thus, the density of the Bi_2O_2. Effects of alternating the elements of both A and B on the electrical properties of these oxide films have been reported [2, 3]. However, the role of the number of BO_6 octahedra between two neighboring Bi_2O_2 layers on the electrical properties has not been emphasized so far. In fact, the synthesis of homologous oxide thin film systems can offer tremendous potential for tailoring the superconducting, ferroelectric and dielectric properties of materials. For example, by preparing the first five members of the $Sr_{n+1}Ti_nO_{3n+1}$ Ruddlesden–Popper homologous series by molecular beam epitaxy (MBE), Haeni et al. revealed that the first member of this series, Sr_2TiO_4, has several potential advantages over the $n = \infty$ member, $SrTiO_3$, in the applications of metal-oxide-semiconductor field-effect transistors (MOSFETs) [4].

In the case of Bi-layered oxides, electrical properties of members with $m = 2, 3, 4$ and 5 have been reported [5–8]. Obviously, naturally existing series provide some novel materials that are stable and can be processed easily. In this paper, we report the electrical properties of $Sr_3Bi_4Ti_6O_{21}$ (SBTi), which is a member of the Bi-layered oxide family with six octahedra between two neighboring Bi_2O_2 layers. Although optical properties of SBTi films were reported [9], there is, as far as we know, no reports on their structural, ferroelectric and dielectric properties. It was suggested that Bi-layered oxides with $m > 5$ could not occur naturally and any attempt to fabricate such an oxide would end in a mixture of the phases $Sr_2Bi_4Ti_5O_{18}$ and $SrTiO_3$ (STO) [10]; however, there is no direct reason to prohibit their occurrence, especially in the form of thin films, which will be discussed below. In fact, several detailed papers on the structures and properties of the higher titanates have been published [11–13]. In this paper, we will report for the first time the ferroelectric and dielectric properties of SBTi thin films fabricated on Pt-coated Si substrates by pulsed laser deposition (PLD).

The SBTi pellets used as PLD targets were prepared by a solid-state reaction with starting materials $SrCO_3$, Bi_2O_3 (in excess of the stoichiometric requirement by 20 mol % initially because of the volatile property) and TiO_2. The mixture of $SrCO_3$, Bi_2O_3 and TiO_2 with ratios of Sr : Bi : Ti = 3 : 4.8 : 6 was ball-milled for 12 h, preheated at 700 °C for 2 h and pressed into pellets; these pellets were then fired at 1050 °C for 2 h. The PLD processes were performed using a Lambda Physik LPX205i KrF excimer laser system of 248-nm radiation and 30-ns pulse width. A pellet was placed in the deposition chamber and a pulsed laser beam with a repetition rate of 5 Hz was focused on the rotated pellet. At 750 °C, SBTi thin films were prepared on $Pt/TiO_2/SiO_2/Si$ substrates

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for 20 min under a flowing oxygen partial pressure of 30 Pa. After deposition, the films were in situ annealed at 750 °C for 10 min under 0.5-atm oxygen pressure. For electrical measurements, Pt top electrodes with 200-μm diameter were deposited onto the surface of the films through a shadow mask at room temperature. Ferroelectric measurements were carried out after post-annealing the films at 750 °C for 30 min under 0.5-atm oxygen pressure.

The SBTi thin films were characterized by X-ray diffraction (XRD) using a Rigaku X-ray diffractometer with nickel-filtered Cu K_α radiation. Surface morphology of the films was recorded by a Nanoscope IIIa atomic force microscope (AFM) (Digital Instruments) and cross-sectional microstructures of the Pt/SBTi/Pt/TiO_2/SiO_2/Si (Pt/SBTi/Pt) configuration were examined by a Philips XL30FEG scanning electron microscope (SEM). Ferroelectric properties were measured by a RT66A and a RT6000HVS ferroelectric test system of Radiant Technologies. A HP 4294A impedance/phase analyzer was used for dielectric measurements.

Figure 1 shows an XRD pattern of the SBTi films deposited on Pt-coated silicon substrates, where orthorhombic structures were used to index the diffraction peaks. It should be noted that no peaks of STO could be detected in the XRD pattern, revealing that the films were not a mixture of $Sr_2Bi_4Ti_5O_{18}$ and STO phases. Our recent careful structural characterization, including cross-sectional high-resolution transmission electron microscopy (HRTEM), of epitaxial SBTi thin films grown on (001) STO single-crystal substrates has revealed the real existence of the SBTi single phase. The results will be shown elsewhere. The peaks of SBTi were indexed by assuming $a = 0.5428$ nm, $b = 0.5438$ nm (according to the standard data of $SrBi_4Ti_4O_{15}$ and other Bi-layered oxides) and $c = 5.700$ nm [9]. The major peaks of (00$\underline{14}$) and (00$\underline{28}$) indicated that the polycrystalline SBTi films were highly c-axis-oriented. The full width at half maximum (FWHM) of the (00$\underline{14}$) peak was 0.25°. The sharp peaks in this XRD pattern suggested that the films are well crystallized. The average grain size in the SBTi films was estimated to be about 34 nm, using the Scherrer equation.

Surface morphology of the films recorded by AFM over an area of 1 μm × 1 μm is shown in Fig. 2. A smooth and dense surface without any cracks was presented. The grain size of the films was only around 40 nm, which was consistent with the value calculated from XRD data. The dominance of near-spherical grains might be consistent with the XRD results that the films were highly c-axis-oriented. Figure 3 shows the SEM cross-sectional morphology of the Pt/SBTi/Pt configuration. It emphasizes that the homogeneous and dense films were column-like grown. The sharp interface between the films and the Pt bottom electrode was revealed. The thickness of the films was determined to be 450 nm.

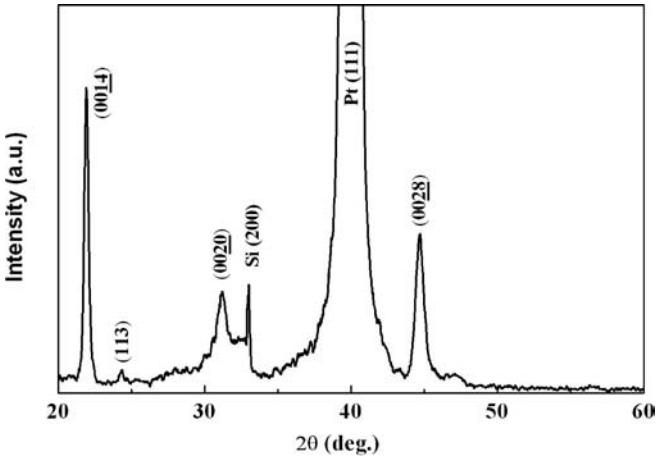

FIGURE 1 XRD pattern of SBTi thin films deposited on Pt-coated Si substrates

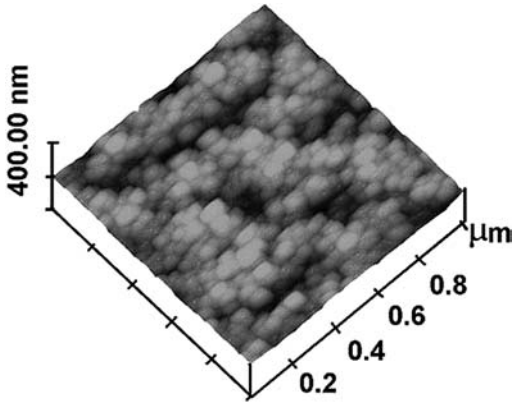

FIGURE 2 Three-dimensional AFM surface morphology of SBTi thin films

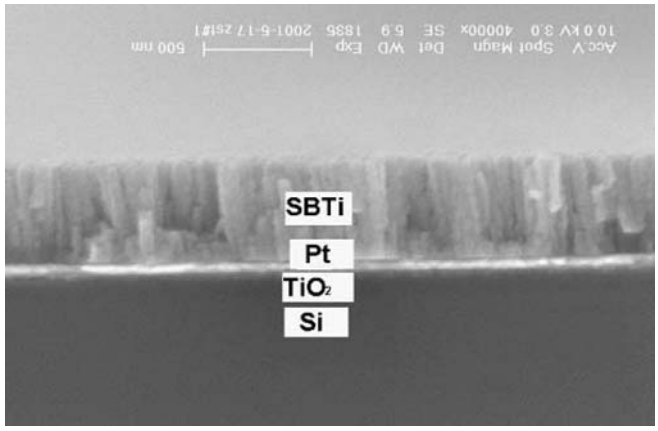

FIGURE 3 Cross-sectional SEM image of the Pt/SBTi/Pt configuration

A typical hysteresis loop of the SBTi films is shown in Fig. 4. With an applied field of 400 kV/cm, the remanent polarization (P_r) and the coercive field (E_c) values were 4.1 μC/cm^2 and 75 kV/cm respectively. The small P_r value might result from the fact that the films were highly c-axis-oriented: it is well known that Bi-layered ferroelectric oxides have the polarization vectors in a–b planes. Other highly c-axis-oriented Bi-layered oxide (such as $BaBi_4Ti_4O_{15}$) thin films also showed such a hysteresis loop with a small P_r [14]. This observation confirmed that the P_r of a Bi-layered oxide film depends greatly on the film orientation.

Fatigue tests were carried out by applying bipolar pulses with about 267 kV/cm (12 V) in amplitude and 50 kHz in frequency to Pt/SBTi/Pt capacitors. A typical fatigue characteristic is shown in Fig. 5. It can be seen that, after 2.2×10^9 switching cycles, the values of the positive non-volatile polarization (P^*–$P^\wedge$) decreased from 1.40 μC/cm^2

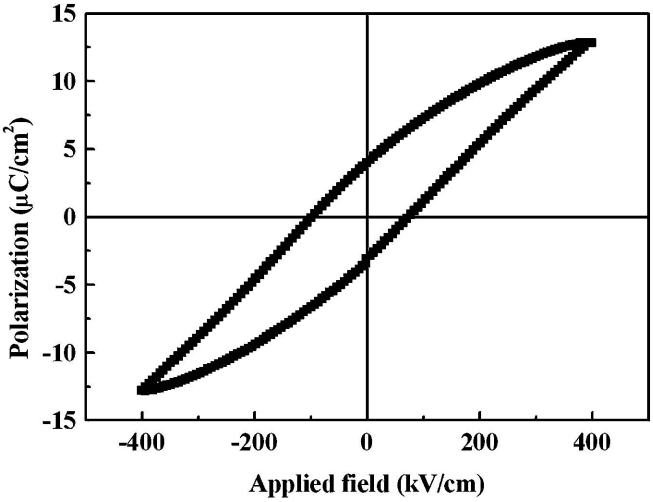

FIGURE 4 $P-E$ hysteresis loops of the SBTi thin films

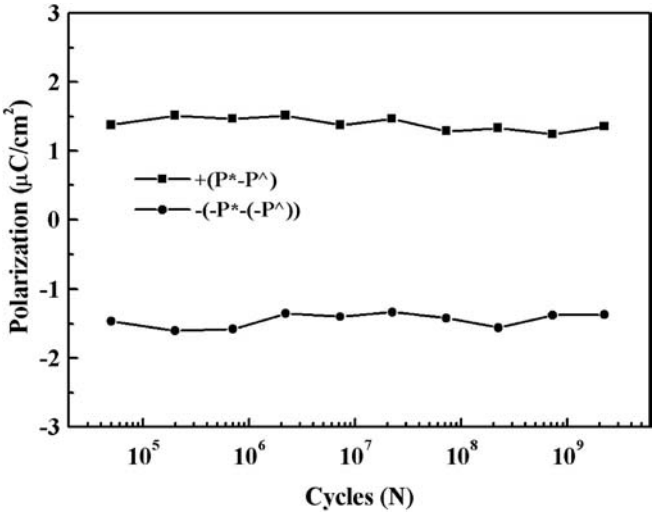

FIGURE 5 Fatigue characteristics of the SBTi thin films

to 1.38 μC/cm^2 and the values of the negative nonvolatile polarization ($-P^*-(-P\hat{})$) decreased from 1.44 μC/cm^2 to 1.37 μC/cm^2. This meant that the film retained at least 95% of its initial polarization. It has been suggested that most of the domain configuration in Bi-layered oxides should be the 180° domains [15]. The excellent fatigue property of SBTi thin films may be due to the 180° domains and the small polarization: charges trapped at a 180° domain boundary can be easily detrapped and a small polarization can reduce the trap depth for charges at the domain boundary. These will result in a small maximum trapped charge density and a low domain-pinning rate, and thus good fatigue characteristics [16]

Figure 6 shows the result of a dielectric and loss tangent measurement on the SBTi thin films. Generally, no severe dispersion was observed. At about 100 kHz, the measured dielectric constant and loss tangent values were 363 and 0.04 respectively. As the frequency was scanned to 2 MHz, the dielectric constant value dropped to 347, about a 6% decrease of the initial value. The loss tangent remained fairly low (about 0.04–0.07) in the frequency range mentioned above

In summary, highly c-axis-oriented SBTi thin films were prepared on Pt-coated silicon substrates. The fact that no STO

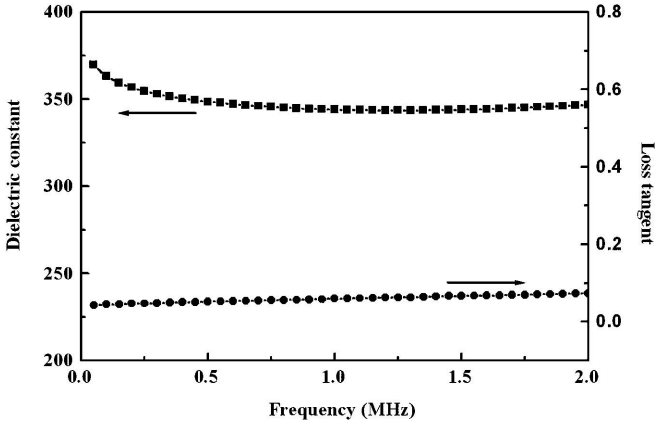

FIGURE 6 Frequency dependency of dielectric constant and loss tangent of the SBTi thin films

peaks could be detected in the XRD pattern indicated the existence of the SBTi single phase. Good ferroelectric properties with P_r and E_c values of 4.1 μC/cm^2 and 75 kV/cm respectively were established experimentally. The small P_r resulted from the fact that the films were highly c-axis-oriented. After 2.2×10^9 switching cycles, the films retained at least 95% of the initial nonvolatile polarization. The 180° domain configuration and the small P_r of SBTi thin films were responsible for the observed excellent fatigue properties. The dielectric constant and loss tangent of the films were measured to be 363 and 0.04 at 100 kHz. These results may be advantageous for NVFRAM and dynamic random access memory (DRAM).

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