$BaBi_4Ti_4O_{15}$ ferroelectric thin films grown by pulsed laser deposition

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(Received 24 August 1998; accepted for publication 14 November 1998)

$BaBi_4Ti_4O_{15}$ (BBiT) is an $n=4$ member of the Bi-layer-structured ferroelectric oxide family (Aurivillius phases). BBiT thin films with preferred orientations have been grown on epitaxial conducting $LaNiO_3$ electrodes on (001) $SrTiO_3$ by pulsed laser deposition. Cross-section electron microscopy analysis reveals that the films consist of c_t-axis oriented regions and mixed a_t- and c_t-axis oriented regions. The mixed a_t- and c_t-axis oriented regions show high surface roughness due to the rectangular crystallites protruding out of the surface, whereas the c_t-axis oriented regions show a smooth surface morphology. In the mixed a_t- and c_t-axis oriented regions, the BBiT films exhibit saturated ferroelectric hysteresis loops with remnant polarization P_r of 2 μC/cm^2 and coercive field E_c of 60 kV/cm and no polarization fatigue up to 10^8 cycles. The regions having c_t-axis orientation with a smooth surface morphology exhibit a linear $P-E$ curve. The results show that the ferroelectric properties of a planar capacitor consisting of BBiT depend on the crystalline orientation of the film. © *1999 American Institute of Physics.* [S0003-6951(99)01204-8]

Ferroelectric materials have innumerable properties related to their spontaneous polarization, for instance, pyro- and piezoelectricity, which are used for various sensors and actuators.[1] The use of ferroelectric thin films brings not only the additional advantage of reduced weight and size, but it allows the fabrication of *integrated* devices which involve switching of the polarization between the two thermodynamically stable states. The development of sophisticated film-synthesis methods providing high-quality films, together with presently existing efforts to find new or alternative solutions for computer memories, makes ferroelectric nonvolatile memories very attractive.[2] Simple perovskite ferroelectric films (such as PZT) on platinized silicon substrates exhibit high polarization fatigue.[3] This problem could be overcome to some extent by replacing the Pt electrodes with conducting oxide electrodes,[4] or by replacing PZT with Bi-based layer-structured ferroelectric oxides, which are known to be free of polarization fatigue up to 10^{12} cycles of polarization.[5,6] These Bi-based layer-structured ferroelectric oxides belong to the Aurivillius family and can be described by the general formula $(Bi_2O_2)^{++}(A_{n-1}B_nO_{3n+1})^{--}$. The high fatigue resistance of these oxides seems to be due to their crystal structure, where n perovskite-like oxygen octahedra are sandwiched between $(Bi_2O_2)^{++}$ layers.

$BaBi_4Ti_4O_{15}$ (BBiT) is a member of the Aurivillius phases with A=(Ba, Bi), B=Ti and $n=4$. The crystal structure of BBiT can be described by an orthorhombic or a pseudotetragonal unit cell. In this letter a pseudotetragonal unit cell is used and it is indicated by the subscript ''*t*.'' The tetragonal lattice parameters of BBiT are $a_t=3.86$ Å and $c_t=41.8$ Å.[7] The anisotropy in the dielectric properties of single-crystalline $BaBi_4Ti_4O_{15}$ (BBiT) and the optical properties of c_t-axis oriented films of $SrBi_4Ti_4O_{15}$ (SBiT), both being $n=4$ members of the Bi-based layer-structured ferroelectric oxide family, have recently been reported.[8,9] The ferroelectric properties of *c*-oriented $Bi_4Ti_3O_{12}$ (BiT) thin films on oxide electrodes have been reported as well.[6] It is desirable to explore the ferroelectric properties of well-oriented thin films of the higher members ($n>3$) of the Bi-layer-structured ferroelectric oxide family. In this letter we report on the orientation-dependent ferroelectric properties of strongly oriented BBiT thin films on conducting epitaxial $LaNiO_3$ (LNO) electrodes grown by pulsed laser deposition (PLD). Epitaxial LNO thin films serving as an oxide electrode for $Bi_2VO_{5.5}$ ($n=1$) have been reported earlier.[10]

BBiT and LNO films were grown by PLD employing a KrF excimer laser ($\lambda=248$ nm). These films were deposited at a laser repetition rate of 5 Hz with a laser pulse energy density of 2 J/cm^2 on single-crystalline (100) $SrTiO_3$ (STO) substrates. Epitaxial LNO electrodes with nominal thickness of 100 nm were grown at a substrate temperature of 825 °C in an oxygen ambient of 300 mTorr. The details of PLD of epitaxial LNO thin films and their properties have been described elsewhere.[11] 400 nm thick BBiT films were deposited *in situ* onto the LNO electrode layer at a substrate temperature of 800 °C in an oxygen ambient of 100 mTorr. After the BBiT film deposition, the samples were cooled to room temperature in 1 Torr of oxygen. The structure of the films was studied by x-ray diffraction (using Philips X'Pert MRD) and cross-section transmission electron microscopy (XTEM). The film morphology was probed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Ferroelectric measurements were carried out on these planar capacitor structures employing a RT66A ferroelectric tester and mercury probe.

BBiT thin films grown on (100) oriented epitaxial LNO electrodes on STO single-crystal substrates show mainly *c*-oriented growth. X-ray diffraction (XRD) θ–2θ scans (not shown here) show $(00l)_t$ peaks of BBiT and a weak $(110)_t$ BBiT peak at 2θ of 32.8°. In Fig. 1, the x-ray pole figure for the $(109)_t$ peak of BBiT is given. The pole figure shows a set (four peaks) of high-intensity peaks at $\Psi=50.2°$ correspond-

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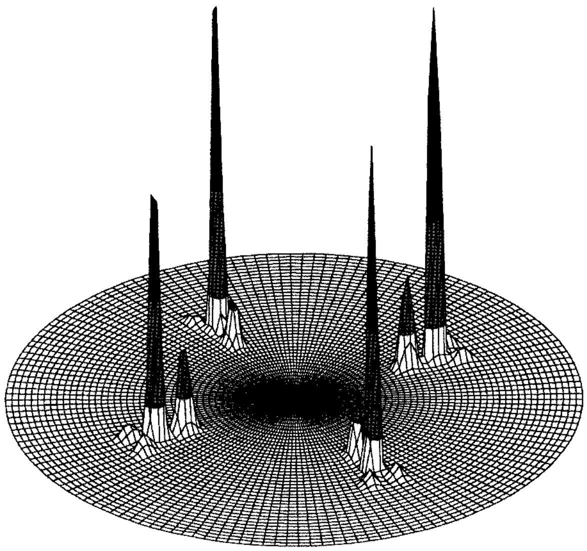

FIG. 1. X-ray pole figure of a BBiT film performed with the $\{109\}_t$ peaks ($2\theta = 30.0°$). The high-intensity peaks ($\psi = 50.2°$) correspond to the c_t-oriented grains and the low-intensity peaks ($\psi = 39.8°$) to the a_t-oriented grains. The very low-intensity (split) peaks ($\psi = 57.0°$) originate from the $(110)_t$-oriented crystallites. The vertical scale is the square root of the measured intensity.

ing to BBiT $(001)_t$, a set of peaks of moderate intensity at $\Psi = 39.8°$ corresponding to $(100)_t$, and a set of very low-intensity peaks at $\Psi = 57.0°$ corresponding to $(110)_t$. The pole figure analysis clearly demonstrates that the BBiT film contains mainly $(001)_t$ and $(100)_t$ oriented grains. More detailed XRD texture analysis shows that $(001)_t$ is parallel to (001) STO in the case of c_t-oriented crystallites and $(100)_t$ is parallel to (001) STO for the a_t-oriented crystallites. The details of these measurements will be provided elsewhere. The lattice parameter c_t calculated from x-ray diffraction is 41.7 Å and is comparable to the reported bulk value.[7]

The SEM images show more or less rectangular-shaped crystallites on the surface of the film in some regions [Fig. 2(a)], whereas other regions show a smooth surface morphology. The rectangular-shaped crystallites are arranged with the long axis along two mutually perpendicular orientations on the substrate plane. The surface morphology was also examined by atomic force microscopy. The AFM images show a surface morphology similar to that observed in SEM. Figure 2(b) shows a topographic line scan of an AFM image taken in a region where SEM revealed the presence of rectangular-shaped crystallites. The AFM line scan shows that the crystallites are protruding out of the smooth background. The AFM images of the regions without the rectangular-shaped crystallites showed highly smooth surface morphology with a root-mean-square (rms) surface roughness of 2.5 nm over a $2.5 \times 2.5\ \mu m^2$ area.

TEM cross-section images and corresponding selected area diffraction (SAD) patterns were taken from those regions where a high density of rectangular-shaped crystallites were observed by SEM and AFM. The XTEM images showed that the electrode layer thickness is about 150 nm and the BBiT film has a thickness of about 400 nm. The BBiT film consists of two sublayers. The lower sublayer (located directly on the LNO electrode) consists of c_t-axis oriented grains as indicated by the $(001)_t$ lattice fringes seen in

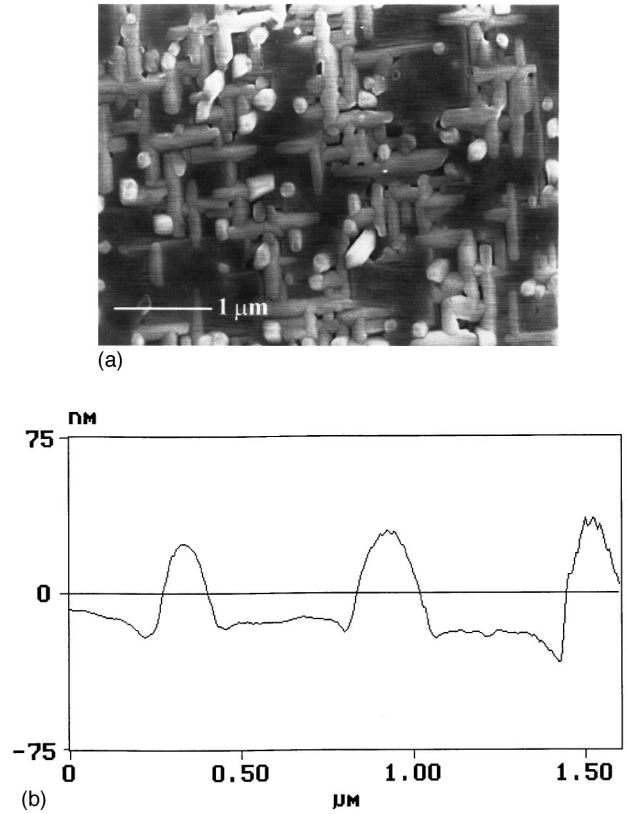

FIG. 2. (a) Scanning electron micrograph of a BBiT film showing rectangular crystallites on the surface; (b) AFM topographic line profile of a BBiT film with rectangular crystallites protruding out of the surface.

the cross-section image (A in Fig. 3). The upper sublayer mainly consists of a_t-axis oriented grains (Fig. 3) and very few c_t-axis oriented grains. The regions with a_t-axis oriented grains (B and C in Fig. 3) possess a high surface roughness, whereas the c_t-axis oriented grains show a smooth flat surface (A′ in Fig. 3). The c_t-axis oriented grains are easily identified by their $(001)_t$ fringes running parallel to the substrate surface. In the a_t-axis oriented grains fringes perpendicular to the substrate surface are observed in region B (Fig. 3). The fringes in the a_t-axis oriented crystallites in region C

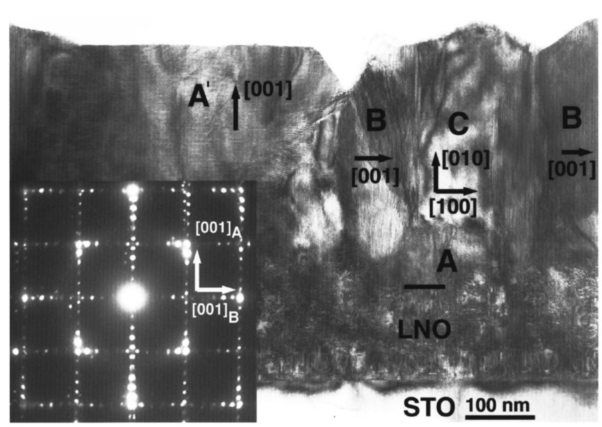

FIG. 3. TEM cross-section image of a BBiT film in the region where rectangular-shaped crystallites were found. The image shows the c_t-axis oriented grains (A,A′) and also the a_t-axis oriented grains (B and C). The inset displays a selected area diffraction pattern corresponding to both c_t- and a_t-axis oriented grains.

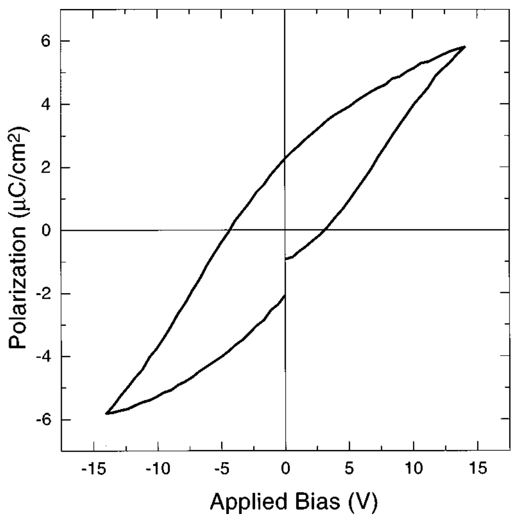

FIG. 4. Ferroelectric hysteresis loop of a film region having a_t-axis oriented crystallites on the surface.

(Fig. 3) are not visible because Bi_2O_2 planes are in the plane of the figure. The inset of Fig. 3 displays a SAD pattern corresponding to both a_t- and c_t-axis oriented grains. From the XTEM results it is inferred that the grains protruding out of the surface are a_t-oriented grains whereas the smooth surface regions are c_t oriented.

Ferroelectric hysteresis measurements were carried out on the BBiT films, separately accessing different regions showing different morphologies by using a Hg probe with contact area of 0.08 mm^2. The a_t- and c_t-oriented $10 \times 10\,mm^2$ film had regions of several mm^2 having only c_t-axis oriented grains with smooth surface and several mm^2 regions with a_t-oriented crystallites embedded in the c_t-oriented film. In the regions with a_t-axis oriented grains the BBiT films exhibit saturated ferroelectric loops with a remnant polarization of 2 $\mu C/cm^2$ and a coercive field of 60 kV/cm (Fig. 4). No polarization fatigue was observed up to 10^8 switching cycles in the region where a_t-axis oriented crystallites were present. No hysteresis loops were observed in the c_t-axis oriented regions. This observation suggests that the macroscopic polarization depends on the degree of a_t-axis orientation in the film.

In the literature it is reported that layer-structured ferroelectric oxides exhibit a high degree of anisotropy in their electrical properties owing to their crystal structure. For instance, a high dielectric constant in the *ab* plane and a comparatively low dielectric constant along the c_t axis have been observed in BBiT single crystals.[8] There is a belief that Bi-layer-structured ferroelectric oxides with even n exhibit no spontaneous polarization along the c_t axis, whereas those with odd n exhibit spontaneous polarization along the c_t axis.[12] Spontaneous polarization has indeed been reported for c-axis oriented BiT ($n=3$) films.[6] On the other hand, Desu *et al.*[13] reported an orientation dependence of the ferroelectric properties of $SrBi_2Ta_2O_9$ (SBT) ($n=2$) thin films grown on Pt electrodes; they observed a decrease in the polarization and coercive field values with an increase in the degree of c_t-axis orientation. Recently, artificial superlattices with the c_t axis normal to the substrate of Bi-based ferroelectric oxides with $n=1-3$ perovskite layers sandwiched between Bi_2O_2 layers were grown by Tabata *et al.*[14] and they reported ferroelectric hystersis loops for $n=1$ or 3, whereas superlattices with $n=2$ showed a linear $P-E$ curve. Based upon the above considerations, it seems that the ferroelectric hysteresis loops obtained in our BBiT films are solely due to a_t-axis oriented crystallites as we do not observe any ferroelectric hysteresis loop in the c_t-axis oriented region of the films. It is, therefore, of technological importance to grow *a*- or *b*-axis oriented epitaxial films of BBiT.

In conclusion, preferentially oriented BBiT thin films have been grown on (100)-oriented epitaxial LNO electrodes. Saturated ferroelectric hysteresis loops with P_r of 2 $\mu C/cm^2$ and E_c of 60 kV/cm have been obtained for the regions with a_t-oriented crystallites, whereas perfect c_t-axis oriented regions exhibit linear $P-E$ curves. The results show that the macroscopic ferroelectric properties of these layer-structured oxide thin films strongly depend on the crystalline orientation of the films.

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