Applied Physics Letters

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Citation: Applied Physics Letters **77**, 3090 (2000); doi: 10.1063/1.1322055
View online: http://dx.doi.org/10.1063/1.1322055
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/77/19?ver=pdfcov
Published by the AIP Publishing

Epitaxial growth of $SrBi_2Nb_2O_9$ on (110) $SrTiO_3$ and the establishment of a lower bound on the spontaneous polarization of $SrBi_2Nb_2O_9$

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(Received 31 March 2000; accepted for publication 6 September 2000)

Epitaxial $SrBi_2Nb_2O_9$ thin films have been grown on (110) $SrTiO_3$ substrates by pulsed laser deposition. Four-circle x-ray diffraction and transmission electron microscopy reveal nearly phase pure epitaxial films with the c axis of the films at 45° with respect to the substrate normal. Electrical characterization is presented for films grown on epitaxial $SrRuO_3$ electrodes. The low-field relative permittivity was 235, the remanent polarization was 11.4 $\mu C/cm^2$, and the dielectric loss was 3.0% for 0.3-μm-thick films. From the remanent polarization and an understanding of the epitaxial geometry, a lower bound of 22.8 $\mu C/cm^2$ was determined for the spontaneous polarization of $SrBi_2Nb_2O_9$. © *2000 American Institute of Physics.* [S0003-6951(00)03844-4]

With the recent interest in the use of ferroelectric thin films for nonvolatile memory and ferroelectric field effect transistors, a number of studies have examined the ferroelectric characteristics of the Aurivillius[1] family of compounds (including the $n=2$ member $SrBi_2Nb_2O_9$).[2,3] Although these materials have received much attention, many of the fundamental properties of these materials have yet to be established. For example, the spontaneous polarization and the complete dielectric tensor of $SrBi_2Nb_2O_9$ have not been experimentally determined, largely due to the fact that either growing single crystals or epitaxial films with appropriate orientations is difficult. It has been shown that $SrBi_2Nb_2O_9$ has a propensity to grow with a c-axis orientation on (001) perovskite-based substrates regardless of deposition parameters, principally due to the narrow window in growth parameter space in which single-phase films can be grown.[4,5] However, because $SrBi_2Nb_2O_9$ (and all members of the Aurivillius homologous series with even n)[6] exhibit mirror inversion symmetry perpendicular to the c axis (and a spontaneous polarization entirely along the a axis),[6] one must investigate films with other orientations to probe the polarization anisotropy. In other words, films must be grown where some projection of the a-axis polarization lies along the same direction as the applied electric field. Indeed, the growth of non-c-axis orientations has been recently demonstrated for some $n=2$ Aurivillius compounds, with substrate choice and orientation (i.e., growth on non-{001}-oriented perovskites[4,7–10] or growth on nonperovskites[11]) being the critical factor. In this study, we employ this strategy and report the growth of $SrBi_2Nb_2O_9$ on (110) $SrTiO_3$ as a means to make a quantitative estimate of the spontaneous polarization.

$SrBi_2Nb_2O_9$ films ~0.3 μm thick were grown *in situ* by pulsed laser deposition using a KrF excimer laser and a single target with a Sr:Bi:Nb atom ratio of 1:2.3:2. Films were grown in a 110 mTorr O_3/O_2 mix (~8% O_3) at a temperature of 877 °C, a fluence of 2–3 J/cm^2, and a 4 Hz pulse rate. Details concerning target fabrication and optimization of the growth of these bismuth-based compounds are given elsewhere.[5]

Heterostructures consisting of an underlying (110) $SrRuO_3$ epitaxial electrode and an epitaxial $SrBi_2Nb_2O_9$ overlayer were prepared to investigate the electrical properties of the $SrBi_2Nb_2O_9$ films. $SrRuO_3$, nearly lattice-matched with $SrTiO_3$ and chemically compatible with both the ferroelectric and substrate, proves to be an excellent choice.[12] $SrRuO_3$ electrodes were grown with a stoichiometric target (99.9% purity, Target Materials, Inc.) at 600 °C and 100 mTorr O_2 with all other growth parameters as described previously for the growth of $SrBi_2Nb_2O_9$. Top platinum electrodes (250 μm diameter) were deposited through a shadow mask by e-beam evaporation at 350 °C.

One of the critical factors that contributes to the utility of using the growth of $SrBi_2Nb_2O_9$ on (110) $SrTiO_3$ to estimate spontaneous polarization is the resulting growth orientation of the ferroelectric. Figure 1 shows a schematic of the observed orientation for the growth of the film. As has been observed in other perovskite-based systems grown on (110) $SrTiO_3$,[13–15] this growth can be alternatively described as (001) film ∥ (001) $SrTiO_3$ which results with the c axis of the $SrBi_2Nb_2O_9$ tilted by 45° with respect to the substrate normal. Atomic force microscopy studies on $SrTiO_3$ (110) substrates that have been heated in an identical manner as the substrates upon which we grow $SrBi_2Nb_2O_9$ films reveal that

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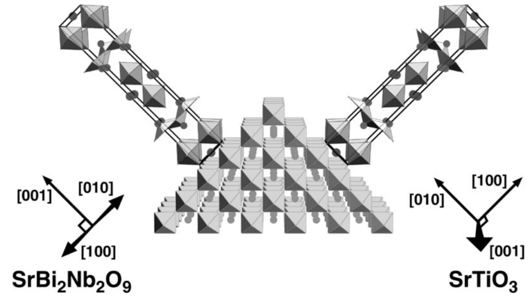

FIG. 1. Schematic showing the observed epitaxial orientation relationship of $SrBi_2Nb_2O_9$ grown on the faceted surface of (110) $SrTiO_3$. The $SrBi_2Nb_2O_9$ is drawn and its unit cell is outlined in its tetragonal state above its Curie temperature. Note that the growth temperature is well above the Curie temperature of $SrBi_2Nb_2O_9$, so the crystallography shown is relevant during nucleation and growth of the epitaxial film. After cooling through the Curie temperature, each of the twins shown is twinned further due to $a-b$ twinning, leading to a total of four expected twin states at room temperature. The orthorhombic axes of only one of the four twin variants of the $SrBi_2Nb_2O_9$ film are drawn. The oxygen coordination polyhedra of the TiO_6 octahedra in the substrate and NbO_6 octahedra and Bi_2O_2 layers in the film are shown.

the (110) $SrTiO_3$ substrate surfaces are faceted with (100) and (010) faces.[16] Other researchers have also reported the formation of (100) and (010) facets on (110) $SrTiO_3$ heated in ultrahigh vacuum to 900 °C or in air to 1350 °C.[17,18] This observation lends credibility to the idea that the epitaxy is actually occurring locally on the (100) and (010) substrate facets as (001) $SrBi_2Nb_2O_9$ ∥ (100) $SrTiO_3$ and (001) $SrBi_2Nb_2O_9$ ∥ (010) $SrTiO_3$. Due to the faceting, the local near-coincident site surface mesh for this growth is the same as for the growth of c-axis oriented $SrBi_2Nb_2O_9$ on {100} perovskite substrates.[4] Such local epitaxy on the (100) and (010) facets has also been reported for the growth of other layered perovskites on (110) $SrTiO_3$ substrates.[19–21] Figure 1 shows the two twin states (ignoring the $a-b$ twining) which are expected for growth on this faceted substrate surface with two-fold symmetry.[22]

With the films growing with their c axis at 45° with respect to the substrate normal there is no low index plane parallel to the surface of the substrate, and consequently, when a θ–2θ x-ray diffraction scan is performed [Fig. 2(a)], the only peaks visible are the substrate reflections. For lower quality films or for films grown on electrodes, where the peaks tend to broaden, the shoulder of the $22\underline{12}$ reflection (at $2\theta \approx 65.4°$) appears, indicating that the film has a near (116) orientation.[23] Figure 2(b) shows a ϕ scan of the $00\underline{10}$ reflection of the same film. This ϕ scan at $\chi \approx 45°$ reveals a film with the two twin variants schematically shown in Fig. 1. The peaks have a full width at half maximum in ϕ of 0.6°. These scans indicate that the in-plane epitaxial relationship can be described as $[\bar{1}10]$ $SrBi_2Nb_2O_9$ ∥ [001] $SrTiO_3$ for these two observed twin variants. The epitaxial orientation of the $SrBi_2Nb_2O_9$ films remained the same when they were grown on $SrRuO_3$ epitaxial electrodes, i.e., ∼(116) $SrBi_2Nb_2O_9$ ∥ (110) $SrRuO_3$ ∥ (110) $SrTiO_3$ and $[\bar{1}10]$ $SrBi_2Nb_2O_9$ ∥ [001] $SrRuO_3$ ∥ [001] $SrTiO_3$. A cross-sectional TEM image of such an epitaxial heterostructure is shown in Fig. 3. The microstructure observed by TEM is described elsewhere.[24]

Based on growths on epitaxial $SrRuO_3$ electrodes, the polarization and dielectric properties of the $SrBi_2Nb_2O_9$ were

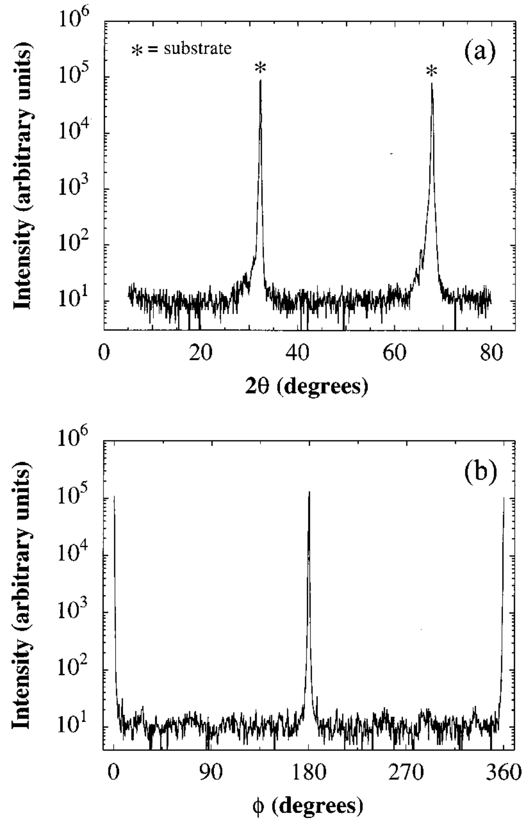

FIG. 2. (a) θ–2θ x-ray diffraction plot of $SrBi_2Nb_2O_9$ grown on a (110) $SrTiO_3$ substrate. Substrate peaks are labeled as (*). Due to the epitaxial orientation relationship, no low index planes are parallel to the substrate surface and only substrate reflections are visible. (b) ϕ scan of the $00\underline{10}$ $SrBi_2Nb_2O_9$ reflection at $\chi = 44.6°$ indicating that the film is epitaxial. ($\chi = 90°$ aligns the diffraction vector to be perpendicular to the plane of the substrate.) $\phi = 0°$ is aligned to be parallel to the $[\bar{1}10]$ in-plane direction of $SrTiO_3$.

investigated. The relative permittivity and loss tangent (tan δ) were measured as a function of applied electric field on an HP 4192A at 10 kHz and a 0.1 V_{rms} oscillation level. The low-field relative permittivity and tan δ were determined to be 235% and 3.0%, respectively. Figure 4 shows a

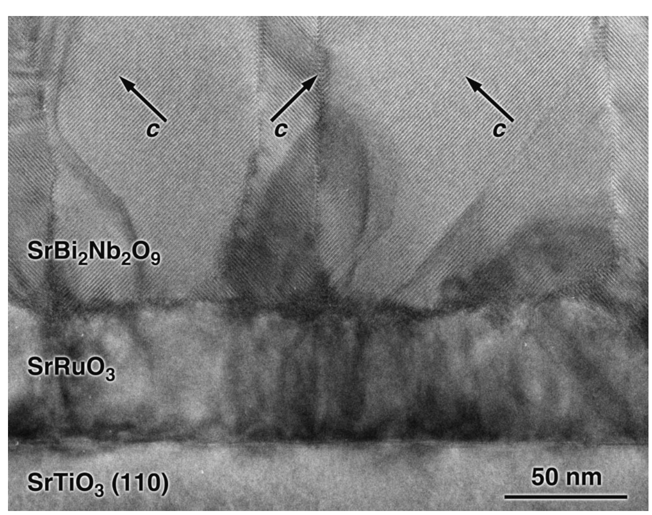

FIG. 3. Cross-sectional TEM image along the [001] $SrTiO_3$ zone axis of the same $SrBi_2Nb_2O_9$/(110)$SrRuO_3$/(110)$SrTiO_3$ film on which the hysteresis curve shown in Fig. 4 was measured. The direction of the c axis is indicated in several of the $SrBi_2Nb_2O_9$ grains, showing the ±45° tilted c-axis twins.

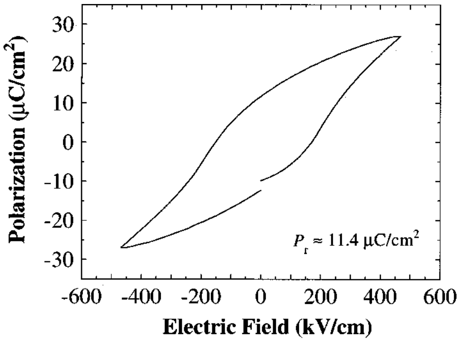

FIG. 4. Polarization-electric field hysteresis curve for $SrBi_2Nb_2O_9$ on an epitaxial (110) $SrRuO_3$ electrode. The remanent polarization is 11.4 $\mu C/cm^2$. A cross-sectional TEM image of the same film on which this hysteresis curve was measured is shown in Fig. 3.

polarization-electric field hysteresis loop of the same $SrBi_2Nb_2O_9$ film measured on an RT6000. The remanent polarization is 11.4 $\mu C/cm^2$.

Hysteresis loops were obtained as a function of maximum applied voltage up to 20 V to ensure convergence of the remanent polarization value. The loop presented in Fig. 4 was taken with a maximum applied voltage of 15 V and shows remanent and maximum polarizations entirely consistent with higher voltage loops, while minimizing concerns of leakage contributions to the displacement current integrated to obtain polarization. Minor-loop and leakage current measurements were also performed, and it was determined that leakage contributes negligible error to the remanent polarization value quoted here.

The special epitaxial geometry allowed a quantitative estimate of the spontaneous polarization of $SrBi_2Nb_2O_9$ to be made from the polarization measurements. With the observed epitaxial relationship, the remanent polarization (P_r) represents a projection of the spontaneous polarization (P_s) in the same direction as the electric field. The relationship between P_r and P_s is given by

$$P_r = P_s(\cos 45°)(\cos 45°) \Rightarrow P_s = 2P_r. \quad (1)$$

From this expression, an estimate of 2×11.4 or 22.8 $\mu C/cm^2$ can be calculated for the spontaneous polarization. Indeed, this estimation serves as a lower bound for this fundamental value, since this calculation assumes that the entire film is switching and that the film is entirely phase pure. The films appear to be free of second phases and fully crystalline, and this is supported by the TEM and x-ray diffraction results. However, a comment on what percentage of the film actually switches cannot be made with certainty.

Unlike other potentially interesting epitaxial orientations where a projection of the spontaneous polarization is along the same direction of the applied electric field, this orientation is special because of the specific angular relationship between the P_r and P_s vectors. Here, the four types of growth twins (two shown in Fig. 1 and an additional two generated within each of those due to $a-b$ twinning) are equivalent in terms of their contributions to the remanent polarization because the projection of the P_s vector for all of the four growth twins is identical (i.e., always involves two rotations of 45°). This is a key simplification, since quantification of the $a-b$ twinning is not required to estimate P_s. Additionally, details concerning the switching nature (through either 90° or 180° reorientation of the polar axis) of the spontaneous polarization can be ignored since both a 90° or a 180° reorientation would result in the same effect on the remanent polarization. This orientation proves to be particularly interesting because of this advantageous geometry, where many of these still unanswered fundamental questions are rendered immaterial to the estimate.

The authors gratefully acknowledge the financial support of the U.S. Department of Energy through Grant No. DE-FG02-97ER45638 for the work performed at Penn State, Contract No. W-31-109-ENG-38 for the work performed at ANL, and use of the ANL Electron Microscopy Center.

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