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Epitaxial growth of non-*c*-oriented ferroelectric $SrBi_2Ta_2O_9$ thin films on $SrTiO_3$ substrates

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Abstract

Non-*c*-axis-oriented $SrBi_2Ta_2O_9$ (SBT) epitaxial thin films with (116)- and (103)-orientations have been grown on Nb-doped (011)- and (111)-oriented $SrTiO_3$ (STO) substrates by pulsed laser deposition, respectively. Analyses of the X-ray diffraction pole figures revealed that the three-dimensional epitaxy orientation relationship $\mathrm{SBT}(001)\|\mathrm{STO}(001)$; $\mathrm{SBT}[1\bar{1}0]\|\mathrm{STO}[100]$ is valid for both cases of SBT thin films, irrespective of STO orientations. The measured remanent polarizations ($2P_r$) of (116)-oriented and (103)-oriented SBT films were 9.6 and 10.4 μC/cm^2, respectively, for a maximum applied electric field of 320 kV/cm. The dielectric constants of (116)- and (103)-oriented SBT were estimated as 155 and 189, respectively. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Dielectric properties; Ferroelectric properties; Films; Perovskites; X-ray methods

1. Introduction

Ferroelectric $SrBi_2Ta_2O_9$ (SBT), a member of the bismuth-layered perovskite family, has a highly anisotropic orthorhombic structure with $a = 0.5531$ nm, $b = 0.5534$ nm, and $c = 2.4984$ nm.[1] Therefore, the ferroelectric properties such as remanent polarization, coercive field, dielectric constant, etc., depend on the crystallographic orientation of the films with respect to the substrate normal. In view of the anisotropic properties of SBT, the growth of non-*c*-oriented SBT films is of particular significance for applications to ferroelectric memory devices, because the vector of the spontaneous electrical polarization in SBT is directed perpendicularly to the *c*-axis, specifically along its *a*-axis.[2,3] This means that a *c*-oriented SBT thin film does not have a polarization component along its film normal (perpendicular to the film plane). Besides the application of these films to ferroelectric random access memories as a capacitor material, the growth of non-*c*-oriented epitaxial SBT films is interesting for fundamental studies of highly anisotropic materials. Moreover, epitaxial SBT films will be required, if the lateral sizes of ferroelectric memory cells will drop down below 100 nm for Gigabit memories.[4,5] Following previous reports on the growth of non-*c*-oriented films on $SrRuO_3$-coated $SrTiO_3$ (STO) substrates by pulsed laser deposition (PLD) and metalorganic chemical vapor deposition,[6,7] we are reporting and comparing here structural and electrical properties of epitaxial (116)- and (103)-oriented SBT films grown by PLD on electrically conductive Nb-doped (011)- and (111)-oriented STO substrates in exactly the same condition (same deposition run).

2. Experimental

The SBT thin films were deposited on STO substrates by PLD using a KrF excimer laser ($\lambda = 248$ nm), operating at a repetition rate of 5 Hz with an energy density of 3.4 J/cm^2 and using a ceramic target of $SrBi_{2.6}Ta_2O_9$. Electrically conductive (011)- and (111)-oriented STO single crystal substrates doped with 0.5% of Nb were used as substrates. The nominal lattice parameter of STO is $a_c = 0.3905$ nm. STO substrates were silver-pasted on a stainless steel substrate holder, which was placed parallel to the target at a distance of 6 cm. The substrate temperature and oxygen chamber pressure were kept at 820°C and 0.4 mbar, respectively, and the films obtained were 250 nm thick. After the SBT film deposition, the

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samples were cooled down to room temperature in 0.4 mbar of oxygen to prevent a bismuth loss in the film. Pt top electrodes with an area of 1.1×10^{-3} cm^2 were deposited by rf-sputtering at room temperature. Details on the sample preparation are available elsewhere.[8] Crystallographic orientation and epitaxial relations were characterized by X-ray diffraction (XRD) $\theta-2\theta$ scans and pole figure measurements using a Philips X'Pert MRD four-circle diffractometer. The polarization versus electric field ($P-E$) and capacitance versus voltage ($C-V$) properties of Pt/SBT/STO:Nb structures were measured by a TF Analyzer 2000 ferroelectric tester (AixACCT) and a HP 4192A impedance analyzer, respectively.

3. Results and discussion

3.1. (116)-Oriented SBT thin films on (011)-oriented STO substrates

Fig. 1 shows an XRD $\theta-2\theta$ scan and a pole figure of a SBT thin film deposited on a (011)-oriented STO substrate. Evidences for the growth of non-*c*-oriented SBT film with a (116) orientation can be found in Fig. 1(a). The full-width at half maximum (FWHM) of the $22\underline{12}$ reflection was 0.25° in a rocking curve θ-scan. The in-plane twist misalignment, $\Delta\phi$, of the (116)-oriented SBT film determined from a ϕ-scan of the SBT00$\underline{10}$ reflection at $\psi = 46.8°$ was 1.06° (Note: $\psi = 90°$ corresponds to the substrate surface being parallel to the plane defined by the incident and reflected X-ray beams).

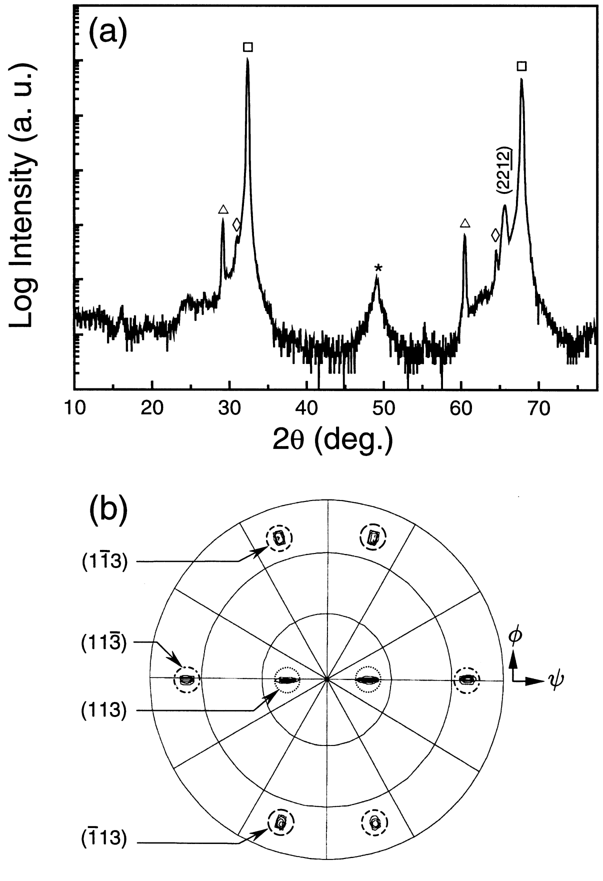

Fig. 1. (a) X-ray $\theta-2\theta$ diffraction pattern and (b) pole figure using the SBT113 reflection ($2\theta = 25.13°$) of SBT thin films on (011)-oriented STO substrates indicating the double-domain configuration [(□): STO substrate, (△): STO-Cu K_β, and (◇): STO-W L_α due to the tungsten contamination of the X-ray target by the tungsten cathode filament]. A peak of an unidentified phase is labeled as (*).

Pole figure analyses were conducted to determine whether the SBT/STO heterostructure is epitaxial and to confirm the SBT crystallographic orientation. The fixed 2θ angle used to record the pole figure is 25.13° corresponding to the SBT{113} planes. The pole figure was plotted with the pole distance angle $\psi = 0°$ (center) to $\psi = 90°$ (rim). As shown in the pole figure of a (116)-oriented SBT film [Fig. 1(b)], we can determine that the (116)-oriented SBT film has been epitaxially grown on the (011)-oriented STO substrate with a double-domain configuration. The innermost two peaks located at $\psi =$ 18° originate from the SBT(113) plane. From this pole figure, it is concluded that the SBT(116) plane is parallel to the substrate surface, because the angle between the (116) and (113) planes of SBT is 18.05°. Moreover, the diffraction peaks from the (11$\bar{3}$) plane and the $(\bar{1}13)/(1\bar{1}3)$ planes are also present at $\psi = 68°$ and 73°, respectively, indicating the double-domain configuration (two-fold symmetry).

In order to characterize the ferroelectric properties of (116)-oriented SBT films, $P-E$ hysteresis curves have been recorded as shown in Fig. 2(a). The remanent polarization ($2P_r$) and the coercive field ($2E_c$) of (116)-oriented SBT films were 9.6 μC/cm^2 and 168 kV/cm, respectively, for a maximum applied electric field of 320 kV/cm. The ferroelectric hysteresis curve was also recorded in $C-V$ measurements as shown in Fig. 2(b). The estimated dielectric constant from the $C-V$ curve at 5 V was 155.

3.2. (103)-Oriented SBT thin films on (111)-oriented STO substrates

Figure 3(a) shows the result of an XRD $\theta-2\theta$ scan of a SBT thin film grown on a (111)-oriented STO substrate. The result reveals a well-defined (103)-oriented SBT film. The FWHM of the 103 reflection was 0.54° in a rocking curve θ-scan. The in-plane twist misalignment of the (103)-oriented SBT film determined from a ϕ-scan of the SBT00$\underline{10}$ reflection at $\psi = 56.4°$ was 0.88°.

In the pole figure of a (103)-oriented SBT film [Fig. 3(b)], six peaks situated at $\psi = 40°$ and 73° were observed. This looks like a six-fold domain configuration, however, a closer inspection shows that it corresponds to a triple-domain configuration: The inner six peaks are corresponding to (113) and (1$\bar{1}$3) planes as marked in the figure and the outer six peaks are related to (11$\bar{3}$) and ($\overline{11}$3) planes, showing that the (103)-oriented SBT thin film has a triple-domain structure.

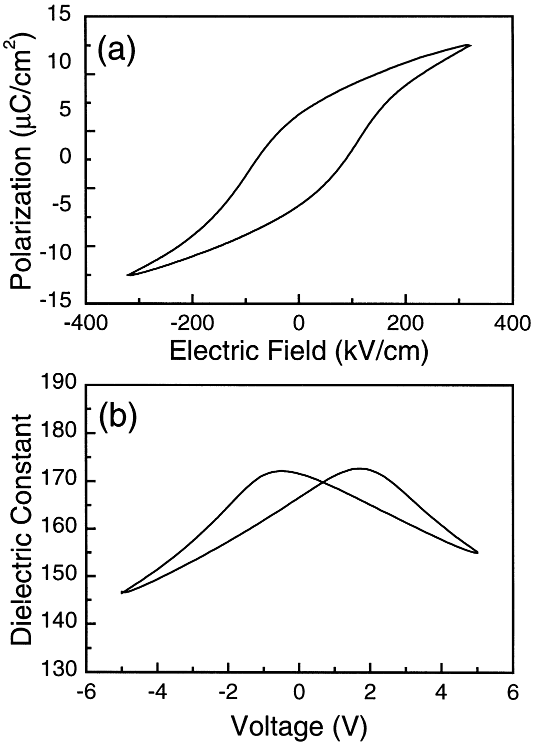

Fig. 2. (a) $P-E$ and (b) $C-V$ hysteresis loops of (116)-oriented SBT films on (011)-oriented STO substrates.

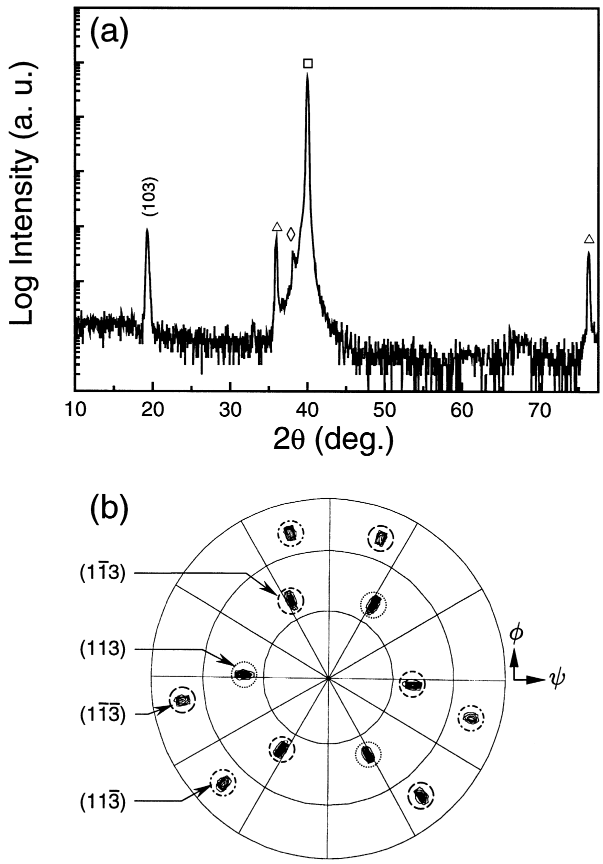

Fig. 3. (a) X-ray $\theta-2\theta$ diffraction pattern and (b) pole figure using the SBT 113 reflection ($2\theta = 25.13°$) of SBT thin films on (111)-oriented STO substrates indicating the triple-domain configuration [(□): STO substrate, (△): STO-Cu K_β, and (◇): STO-W L_α].

Fig. 4(a) shows a ferroelectric hysteresis loop of a (103)-oriented SBT film, revealing a remanent polarization $2P_\mathrm{r} = 10.4$ μC/cm^2 and a coercive field $2E_\mathrm{c} = 104$ kV/cm. As it can be seen in Fig. 4(b), the (103)-oriented SBT film had a higher dielectric constant than the (116)-oriented SBT film. The estimated dielectric constant of the (103)-oriented SBT film at 5 V was about 189.

3.3. Epitaxial orientation relationship and electrical anisotropy

Summarizing the results of Figs. 1 and 3, both the two-dimensional epitaxial relationships between the SBT films and their corresponding STO substrates can be written as follows:

$$\mathrm{SBT}(116)\|\mathrm{STO}(011);\ \mathrm{STB}[1\bar{1}0]\|\mathrm{STO}[100] \tag{1}$$

$$\mathrm{SBT}(103)\|\mathrm{STO}(111);\ \mathrm{SBT}[010]\|\mathrm{STO}[\bar{1}10]. \tag{2}$$

These relationships are, however, not unique because grains of the growing film can grow in various variants allowed by the crystallographic symmetry of the substrates, as indicated in this study. The rotations crystallographically allowed are 180° for STO(011) (double-domain configuration) and 120° for STO(111) (triple-domain configuration). A three-dimensional representation of the relationships (1) and (2) shows that they indeed correspond to only one and the same three-dimensional orientation relationship, which can be applied to both substrates with (011) or (111) orientations, as shown in Fig. 5. This three-dimensional orientation relationship reads

$$\mathrm{SBT}(001)\|\mathrm{STO}(001);\ \mathrm{SBT}[1\bar{1}0]\|\mathrm{STO}[100]. \tag{3}$$

This epitaxial orientation relationship is also found in (001)-oriented SBT films on (001)-oriented STO substrates. Details on the description of these crystallographic orientation relationships have been published before.[8]

Regarding the electrical anisotropy of the SBT films of different orientations with respect to the substrate surface, information about the spontaneous polarization along the *a*-axis of SBT can be obtained by knowing that the spontaneous polarization of SBT is lying along the *a*-axis, and that the angles between the spontaneous polarization and the (116) and (103) planes are about 31° and 56°, respectively. According to these angles, it was expected that the (103)-oriented SBT film has an about 1.6 times larger polarization value than that of the (116)-oriented film. However, the measured remanent polarization values of (116)- and (103)-oriented SBT films did not reveal such a large difference. The reason may be both a

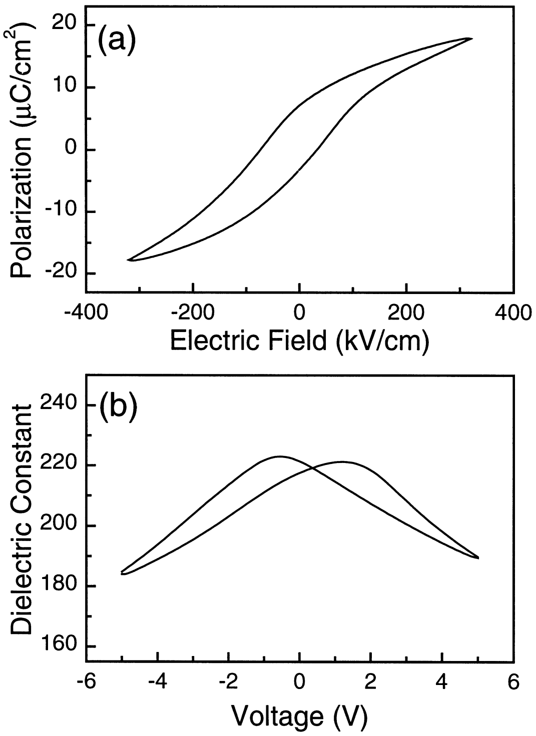

Fig. 4. (a) $P-E$ and (b) $C-V$ hysteresis loops of (103)-oriented SBT films on (111)-oriented STO substrates.

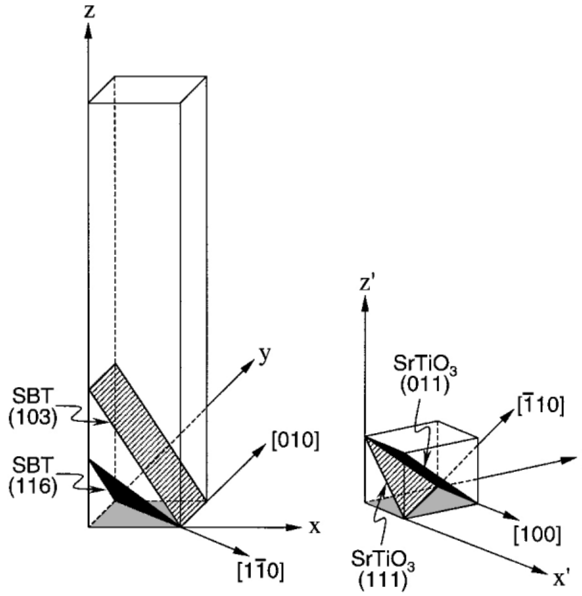

Fig. 5. Three-dimensional schematic drawing of the SBT and STO unit cells. The STO unit cell is rotated 45° in-plane with respect to the SBT unit cell.

higher strain at the interface occurring from the larger lattice mismatch between film and substrate, and a worse electric contact due to the rougher surface morphology of the (103)-oriented film on STO(111) compared to the (116)-oriented film on STO(011).[8] However, the values of the saturation polarization of (116)- and (103)-oriented SBT films better correspond to the expected relation. Overall, the results of $P-E$ and $C-V$ characteristics illustrate well the electrical anisotropy of the ferroelectric properties of SBT films in correspondence to their different crystallographic orientations.

4. Conclusions

We have deposited non-c-oriented SBT thin films by PLD on (011)- and (111)-oriented STO single crystalline substrates. The epitaxial relations were SBT(116)||STO(011) and SBT(103)||STO(111) as well as SBT$[1\bar{1}0]$|| STO[100] for both orientations. An electrical anisotropy of the remanent polarization and the dielectric constant related to the crystallographic orientations of the films was found. The remanent polarizations ($2P_\mathrm{r}$) of (116)- and (103)-oriented SBT films were 9.6 and 10.4 μC/cm^2 for a maximum applied electric field of 320 kV/cm, and the dielectric constants of (116)- and (103)-oriented SBT films were 155 and 189, respectively.

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