Direct Comparison of Structural and Electrical Properties of Epitaxial (001)-, (116)-, and (103)-Oriented $\text{SrBi}_2\text{Ta}_2\text{O}_9$ Thin Films on SrTiO_3 and Silicon Substrates

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ABSTRACT

Anisotropies of the properties of the bismuth-layered perovskite $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) have been investigated using epitaxial thin films grown by pulsed laser deposition both on conducting Nb-doped SrTiO_3 (STO) single crystal substrates and on Si(100) substrates. It has been found that the three-dimensional epitaxy relationship $\text{SBT}(001)\parallel\text{STO}(001)$; $\text{SBT}[1\bar{1}0]\parallel\text{STO}[100]$ can be applied to all SBT thin films on STO substrates of (001), (011), and (111) orientations. An about 1.7 times larger remanent polarization was obtained in (103)-oriented SBT films than in that of (116) orientation, while the (001)-oriented SBT films revealed no ferroelectricity along their c -axis. Non- c -axis-oriented SBT films with a well-defined (116) orientation were also grown on silicon substrates for the first time. They were deposited on Si(100) covered with a conducting SrRuO_3 (110) bottom electrode on a YSZ(100) buffer layer.

INTRODUCTION

Getting epitaxial $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) films ($a = 0.5531$ nm, $b = 0.5534$ nm, and $c = 2.4984$ nm [1]) is an important issue for applications in high-density ferroelectric random access memories (FRAMs). Epitaxial films are needed to overcome the problems related to the lack of uniformity in polycrystalline films [2]. The latter arise, because in high-density memories the lateral sizes of the individual structures approach both the sizes of the grains in polycrystalline films and the size of the ferroelectric domains. One solution to circumvent these non-uniformity problems is to use epitaxial thin films. As the vector of the spontaneous polarization ($\mathbf{P}_s$) in SBT is directed perpendicularly to the c axis, specifically along its a axis, the growth of non- c -axis-oriented SBT films is of particular significance for applications to planar-capacitor-type FRAMs. The epitaxial growth of SBT films both with c -axis and non- c -axis orientations was investigated on single crystal substrates such as SrTiO_3 (STO), LaSrAlO_4 , etc. [3-5]. Particularly, the epitaxial orientation relationship of either SBT or $\text{SrBi}_2\text{Nb}_2\text{O}_9$ (SBN) films grown on (011)- and (111)-oriented STO substrates has been debated, for instance whether the (001) plane of SBT or SBN films is exactly parallel to the (001) plane of STO substrates in the non- c -axis-oriented SBT/SBN films with (116) and (103) orientations on STO(011) and STO(111) substrates [3-5], or whether a small deviation occurs. In this work, we report the epitaxial orientation relationship investigated by means of x-ray diffraction ϕ scans as well as a comparison between the structural and electrical properties of c -axis and non- c -axis-oriented SBT films grown on STO and on Si(100) substrates. For the application of epitaxial films in high-density ferroelectric nonvolatile memories, non- c -axis-oriented SBT films *on silicon* will be needed.

EXPERIMENTAL

The deposition conditions used for the film growth along with the various characterization methods are described in detail elsewhere [5,6]. Briefly, the 250 nm thick SBT films were grown both on single crystalline Nb-doped STO with (001), (011), and (111) orientations and on yttria-stabilized ZrO_2 -buffered (YSZ-buffered) Si(100) substrates covered with conducting SrRuO_3 (SRO) bottom electrodes. All the films were grown by pulsed laser deposition using a KrF excimer laser ($\lambda = 248$ nm). Pt top electrodes with an area of $1.1 \times 10^{-3} \text{ cm}^2$ were deposited by rf-sputtering at room temperature through a stainless steel shadow mask. After top electrode deposition, the samples were annealed at 750°C for 30 min. in an oxygen ambient to stabilize the contact between SBT and Pt. To characterize the structural and electrical properties, x-ray diffraction (XRD), cross-sectional transmission electron microscopy (TEM), scanning force microscopy (SFM), and a TF2000 thin film analyzer (AixACCT) were used.

EPITAXIAL (001)-, (116)-, AND (103)-ORIENTED SBT FILMS ON STO SUBSTRATES

Figure 1 shows XRD ϕ scans of the (001)-, (116)-, and (103)-oriented SBT films on (001)-, (011)-, and (111)-oriented STO substrates, respectively. Details on θ - 2θ and pole figure scans were published elsewhere [5]. In order to record the patterns, the reflections of SBT(113) and SBT(0010) were used at $\psi = 65^\circ$, 46.5° , and 55.8° , respectively. In the case of (001)-oriented SBT films on (001)-oriented STO substrates, the SBT(001) plane is exactly parallel to the STO (001) plane satisfying the epitaxy relationship $\text{SBT}(001) \parallel \text{STO}(001)$; $\text{SBT}[1\bar{1}0] \parallel \text{STO}[100]$. For non- c -axis-oriented epitaxial films, the (001) planes of (116)- and (103)-oriented SBT films are *not* exactly parallel to the STO(001) planes of (011)- and (111)-oriented STO (in which case we

Figure 1. XRD ϕ scans of the SBT films on (a) (001)-, (b) (011)-, and (c) (111)-oriented STO substrates. $\psi = 0^\circ$ corresponds to the substrate surface, perpendicular to the plane defined by the incident and reflected x-ray beams.

would have $\psi = 45^\circ$ and 54.7° , resp.), as shown in Figs. 1(b) and 1(c). These angle deviations of 1.5° and 1.1° correspond to the tilt angle between the SBT(001) plane and the underlying STO(001) plane for (116)- and (103)-oriented SBT films on (011)- and (111)-oriented STO, respectively. Therefore, since the (116), respectively (103) planes are *exactly* parallel to the STO(011), respectively STO(111) planes, small angular deviations up to $\sim 2^\circ$ from the three-dimensional unique epitaxy relationship $\text{SBT}(001) \parallel \text{STO}(001)$; $\text{SBT}[1\bar{1}0] \parallel \text{STO}[100]$ have to be taken into consideration, if the latter is applied to all SBT films on STO substrates of (001), (011), and (111) orientations.

Due to the tilt of the c axis of SBT films with respect to the substrate surface, the directions of the vector $\mathbf{P}_s$ of the spontaneous polarization in (001)-, (116)-, and (103)-oriented SBT films are 90° , $\sim 59^\circ$, and $\sim 34^\circ$ away from

Figure 2. Schematic drawing of polarization components of the growth twins of (a) (001)-, (b) (116)-, (c) (103)-oriented SBT thin films, and the *a-b* twins of (d) (001)-, (e) (116)-, and (f) (013)-oriented films on (001)-, (011)-, and (111)-oriented STO substrates, respectively. The vertical components of the spontaneous polarization ($P_{\perp}$) with respect to the substrate surface are represented as thick solid arrows.

the substrate normal, respectively. Therefore, the polarization of SBT films can be estimated by comparing the recorded ferroelectric hysteresis loops using SBT films having different orientations, assuming full switching. The components of $\mathbf{P}_s$ perpendicular to the substrate surface are proportional to the values of $P_{\perp}^{001} = |\mathbf{P}_s| \cdot \cos 90^\circ = 0$, $P_{\perp}^{116} = |\mathbf{P}_s| \cdot \cos 59^\circ = 0.5|\mathbf{P}_s|$, and $P_{\perp}^{103} = |\mathbf{P}_s| \cdot \cos 34^\circ = 0.8|\mathbf{P}_s|$. Accordingly, the *c*-axis-oriented SBT film reveals a zero normal polarization and the (103)-oriented SBT film has an about 1.7 times larger normal polarization value than the (116)-oriented film as schematically shown in Figs. 2(a)–2(c).

Figure 3 (left) shows the ferroelectric P – E hysteresis loops of (001)-, (116)-, and (103)-oriented SBT films. In the case of (001) orientation, the film reveals no ferroelectricity in the direction normal to the film [Fig. 3 left(a)]. Moreover, an about 1.7 times higher remanent

Figure 3. P – E (left) and C – V (right) hysteresis loops of (a) (001)-, (b) (116)-, and (c) (103)-oriented SBT films. The remanent polarization values of (116)- and (103)-oriented films are 4.3 and 7.4 $\mu\text{C}/\text{cm}^2$, respectively, exhibiting a ratio of their remanent polarization (P_r^{103}/P_r^{116}) of ~ 1.7 .

polarization was recorded for the (103)-oriented SBT film than for the (116)-oriented SBT film [Figs. 3 left(b) and (c)]. The ratio of polarization values, $P_r^{103}/P_r^{116} \approx 1.7$, agrees well with the calculated value even though the absolute polarization values are lower than expected, *cf.* Refs. 3 and 4. Please note that the direct comparison is valid, and the experimental ratio is so nicely consistent with the computed one, because our samples were deposited on substrates having different orientations during the same run, in exactly *the same conditions*.

Dielectric constants of all SBT films on (001)-, (011)-, and (111)-oriented STO substrates were calculated by recording C - V curves as shown in Fig. 3 (right). Like the P - E curves, no hysteresis loop was observed in the case of the c -axis-oriented SBT film [Fig. 3 right(a)]. Non- c -axis-oriented SBT films [Figs. 3 right(b) and (c)] exhibited ferroelectric hysteresis loops showing a higher dielectric constant than the c -axis-oriented SBT film. The calculated dielectric constants of (001)-, (116)-, and (103)-oriented SBT films measured at 5 V in a direction normal to the film were about 133, 155, and 189, respectively.

Twinning of a and b axes in SBT has not yet been reported. The difference of lattice parameters between a and b is too small (~ 0.3 pm) to evidence it by XRD analyses. However, exactly because of this very small difference, and due to the fact that no large displacements are required to "switch" the two axes, some twinning must exist. Moreover, since the polarization is directed along the a axis, it is most probably influenced by an applied electric field. We have tried to find an evidence of the a - b twins by piezoresponse-SFM using SBT films grown on STO(111) substrates. The reason to use the SBT film on the STO(111) is that for (001)-oriented SBT films, both a and b axes are lying parallel to the substrate surface [Figs. 2(a) and 2(d)], and for (116)-oriented SBT, the a and b axes both are lying 31° away from the substrate surface, thus having a component along the normal direction, but for symmetry reason being not distinguishable [Figs. 2(b) and 2(e)]. In the case of (103)-oriented SBT, the a axis ($\mathbf{P}_s$ vector direction) is lying 56° away from the substrate surface and the b axis is lying parallel to the substrate surface. But, if we consider that a - b twinning is present, (013)SBT has its a axis lying parallel to the substrate surface and its b axis 56° away from the substrate surface. In this case, the film has no component of the polarization normal to the film and cannot reveal ferroelectricity along the substrate normal [Fig. 2(f)]. These two types of behavior were qualitatively confirmed by local in-plane and out-of-plane hysteresis loops recorded by piezoresponse-SFM using two different SBT grains of a (103)-oriented SBT film as shown in Fig. 4. In Fig. 4(a), a *higher* piezoresponse along the out-of-plane direction was recorded than along the in-plane direction. On the other hand, in Fig. 4(b), a *lower* piezoresponse along the out-of-plane direction was recorded than

Figure 4. Local piezoresponse hysteresis loops of (a) (103)- and (b) (013)-oriented SBT grains exhibiting evidence of the presence of the a - b twinning of SBT films.

along the in-plane direction. Therefore, we can infer that the former piezoresponse was recorded from a (103)-oriented SBT grain and the latter one was recorded from a (013)-oriented SBT grain revealing an *a-b* twinning of SBT films.

NON-*c*-AXIS-ORIENTED SBT FILMS ON Si(100) SUBSTRATES

Figure 5. X-ray diffraction (a) θ - 2θ scan and (b)–(e) ϕ scans of a SBT/SRO/YSZ/Si(100).

is comparable to the mismatch of 8.1% along the SRO<110> or YSZ<100> directions.) Since there are four positionings to arrange the respective diagonals, four different azimuthal orientations of the (110)-oriented SRO grains, or four variants, result exhibiting characteristic angles of 19.5° . Due to the two-fold positioning of SBT variants on each azimuthal SRO variant,

Figure 6. SFM topography image of a (116)-oriented SBT thin film on SRO(110)/YSZ(100)/Si(100).

As discussed in the introduction, non-*c*-axis-oriented SBT films will be of practical importance *only* if they are grown on a technologically relevant substrate, such as silicon. We succeeded to grow (116)-oriented SBT films on a Si-based substrate, using a (110)-oriented SrRuO₃ (SRO) electrode. Figure 5(a) shows an XRD θ - 2θ scan of a SBT(116)/SRO(110)/YSZ(100)/Si(100) heterostructure. The ϕ scans in Figs. 5(b)–5(e) demonstrate the perfect in-plane orientations of SBT, SRO, and YSZ on Si(100). The SRO layer [Fig. 5(d)] and the SBT film [Fig. 5(e)] display a characteristic peak splitting of $\Delta\phi \approx 20^\circ$. An equivalent azimuthal angle of $\sim 20^\circ$ between neighboring SBT grains was observed in the surface morphology of the (116)-oriented SBT films by SFM (Fig. 6). The reason for the presence of this azimuthal angle, as well as for the observed peak splitting in the ϕ scans, is a specific “*diagonal rectangle-on-cube*” epitaxy relationship of SRO (110) on YSZ(100) minimizing the lattice mismatch as schematically shown in Fig. 7. (The lattice mismatch along the diagonal direction is -6.3% , which

Figure 7. Schematic of the *diagonal rectangle-on-cube* epitaxy of SRO(110) on YSZ(100): (a) YSZ(100), (b) SRO(110), and (c) four variants of SRO on YSZ.

Figure 8. P - E hysteresis loops of a Pt/STB(116)/STO(110) capacitor.

the STB film has *eight* azimuthal variants, which again exhibit characteristic angles of $\sim 20^\circ$. The following orientation relationship has been deduced from the XRD investigations: STB(116)||STO(110)||YSZ(100)||Si(100); STB[110]||STO[100], and STO[111]||YSZ<110>||Si<110> including four azimuthal STO orientations and eight corresponding azimuthal STB orientations. Both the STO and STB grains corresponding to the different azimuthal variants can be visualized by cross-section TEM images (not shown here). The grains are ~ 50 nm in lateral size, and the azimuthal STB domain pattern replicates the one in the STO layer. The STB/STO interface has a characteristic roof-like morphology while the other interfaces are plane and sharp [6].

P - E hysteresis loops of a (116)-oriented STB film are shown in Fig. 8. The loops were recorded before a fatigue test, and after 10^{11} switching cycles using 1 MHz fatigue pulse at 5 V, respectively. The remanent polarization ($2P_r$) and the coercive field ($2E_c$) were about $12 \mu\text{C}/\text{cm}^2$ and 120 kV/cm, respectively, for a maximum electric field of 420 kV/cm. The film revealed excellent fatigue endurance even after 10^{11} switching cycles.

CONCLUSIONS

Anisotropies in the ferroelectric properties of c -axis- and non- c -axis-oriented STB films were investigated. The (103)-oriented STB films exhibited an about 1.7 times larger out-of-plane polarization component than the (116)-oriented STB films, while the (001)-oriented STB films exhibited no component of the polarization along their c -axis direction. An evidence of a - b twinning in (103)-oriented STB films was found by local SFM piezoresponse analysis. Moreover, (116)-oriented STB films have been successfully grown on STO(110)/YSZ(100)/Si(100) substrates. A specific diagonal-type rectangle-on-cube epitaxy of STO on YSZ enables the growth of non- c -axis-oriented STB films on Si substrates.

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