Growth, Structure, and Properties of Uniformly $a$-Axis Oriented Ferroelectric Bi$_{3.25}$La$_{0.75}$Ti$_3$O$_{12}$ Thin Films on Si(100) Substrates

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ABSTRACT

Uniformly $a$-axis-oriented, epitaxially twinned Bi$_{3.25}$La$_{0.75}$Ti$_3$O$_{12}$ (BLT) thin films having the major spontaneous polarization entirely along the film normal were grown by pulsed laser deposition on yttria-stabilized zirconia-buffered Si(100) substrates covered with very thin SrRuO$_3$ bottom electrodes. Using SrRuO$_3$ bottom electrodes of a specific low thickness in combination with a relatively high growth rate and a high oxygen pressure, the volume fraction of the BLT (100) orientation, which is competing with the BLT (118) orientation, was increased up to 99%. In this way the growth of fully $a$-axis-oriented BLT epitaxial films was achieved, attaining a remanent polarization of 32 $\mu$C/cm$^2$. Initial fatigue experiments indicated hardly any fatigue after $10^9$ switching cycles.

INTRODUCTION

Ferroelectric films of bismuth-layered perovskite compounds like SrBi$_2$Ta$_2$O$_9$ (SBT) or (Bi$_x$La)$_4$Ti$_3$O$_{12}$ (BLT) are important for future high-density non-volatile ferroelectric random access memories (NV-FRAMs) [1-3]. Though commercial low-density memories made of polycrystalline SBT films are already in use, the integration of Bi-layered type ferroelectric films into the silicon technology and the increase of memory density (up to the Gbit-size range) remain a challenge. In particular, the growth of uniformly oriented films on Si(100) substrates is significant, because such films will be required, if the lateral size of ferroelectric memory cells will drop down to below 100 nm for Gbit memories [2,4]. This cell size being of the order of the grain size of polycrystalline films, the arising non-uniformity problems with randomly oriented films [5] can be solved by using uniformly oriented films.

If the film is to be used in a ferroelectric thin-film capacitor geometry, the presence of a non-zero polarization component perpendicular to the film plane is essential. This presence is, however, not trivial, because the bismuth-layered perovskite compounds strongly prefer to grow in the $c$-axis orientation but the vector of the spontaneous polarization is (almost or entirely) perpendicular to the $c$-axis in these materials. As a consequence non-$c$-axis oriented films should be grown, particularly on Si(100). The growth of non-$c$-axis oriented SBT, SrBi$_2$Nb$_2$O$_9$ (SBN) or Bi$_4$Ti$_3$O$_{12}$-based bismuth-layered perovskite films on complex-oxide single crystal substrates has been reported by several groups [6-14]. The growth of non-$c$-axis oriented Bi-layered perovskite films on electroded Si(100) substrates was achieved only very recently [15-21]. Mostly thin SrRuO$_3$ bottom electrodes were used on Si(100) [15-20]. Sometimes, however, thin platinum electrodes on Si(100) were applied [21].

Since non-$c$-axis oriented bismuth-layered perovskite films with an inclined polarization vector, like (116)-oriented SBT films, suffer from certain shortcomings of crystallographic origin
[22]. \(a\)-axis oriented films would be much more favourable. Their growth is, however, not trivial, due to the inherent tendency of \(Bi\)-layered perovskite films to grow in the \(c\)-axis orientation.

La-substituted bismuth titanate \(Bi_{3.25}La_{0.75}Ti_3O_{12}\) (BLT), a rather new bismuth-layered perovskite material [3], has both a high fatigue resistance and a high remanent polarization, thus potentially being able to replace SBT and PZT. In view of these properties, the growth of \(a\)-axis oriented BLT thin films on Si(100) should be considered an important step forward towards high-density NV-FRAMS. Here we report on the growth, structure and properties of uniformly \(a\)-axis oriented BLT films on buffered and electroded Si(100) substrates. Details of the growth conditions have recently been (or will shortly be) published [19,20,22].

EXPERIMENTAL DETAILS

The YSZ buffer layers, the \(SrRuO_3\) electrode layers, and the BLT films were all grown by pulsed laser deposition (PLD) not breaking the controlled atmosphere conditions in between. An excimer laser (KrF; wavelength 248 nm) was used at a repetition rate of 2 to 10 Hz to ablate corresponding pressed powder targets in a pure oxygen atmosphere. The targets used for deposition of BLT were rich in bismuth. Substrate temperatures between 650 °C and 825 °C, laser fluences between 1.7 and 4.0 J/cm\(^2\), and oxygen pressures between 30 and 100 Pa were applied. The deposition conditions for each of the layers or films were carefully optimized. For details, see [15,19,20]. The thickness of the YSZ buffer layer was 60 nm. The one of the \(SrRuO_3\) electrode layer was optimized in a range between 10 nm and 50 nm. The thickness of the BLT films ranged from 250 nm to 1 µm. For the electrical characterization, Pt top electrodes with a diameter of 100 µm were r.f. sputter-deposited at R.T. After top electrode deposition, the samples were annealed at 650 °C for 30 min to stabilize the contact between the ferroelectric film and the Pt electrode.

The entire heterostructures were structurally characterized by X-ray diffraction (XRD) using a Philips X’Pert MRD four-circle diffractometer, by atomic force microscopy (AFM) using a Digital Instruments D5000 microscope in tapping mode, and by transmission electron microscopy (TEM) using a JEOL 4010 high-resolution transmission electron microscope (HRTEM). The ferroelectric properties were evaluated using a ferroelectric tester (TF Analyzer 2000, aixACCT). Polarization vs. electric field curves were recorded at a frequency of 100 Hz or 200 Hz, and fatigue endurance was determined at a frequency of 10 kHz.

RESULTS AND DISCUSSION

Crystallographic background

Crystallographic indexing in this work is based on the following unit cells, keeping in mind that two of them (\(Bi_4Ti_3O_{12}\); \(SrRuO_3\)) are approximatives of the proper unit cells. (Data are based on well-known work of other authors and can also be found in the JCPDS-ICDD files.)

\(Bi_4Ti_3O_{12}\): pseudo-orthorhombic unit cell, \(a = 0.545\) nm, \(b = 0.541\) nm, and \(c = 3.283\) nm;
\(SrRuO_3\): pseudo-cubic unit cell, \(a = 0.393\) nm;
\(YSZ\): cubic unit cell, \(a = 0.514\) nm;
\(Si\): cubic unit cell, \(a = 0.5431\) nm.
Growth of $a$-axis oriented BLT films

A key experience that lead us to the basic idea of how to grow $a$-axis oriented BLT films was the observation that during PLD growth of SrBi$_2$Ta$_2$O$_9$ films onto the model substrate SrLaGaO$_4$(110), part of the film was growing in a (100) orientation, this orientation “competing” with the common (116) orientation [12]. After analyzing this observation we were able to make reasonable assumptions on conditions favouring the (100) orientation of BLT films as follows. As we knew before, BLT films grow in the (118) orientation on non-strained, 50 nm thick SrRuO$_3$(110) bottom electrodes [13]. The latter were grown on YSZ(100) buffer layers on Si(100), whereby the particular mutual crystallographic orientation of SrRuO$_3$ and YSZ involved a negative misfit, i.e. smaller interplanar SrRuO$_3$ lattice spacings compared to the corresponding lattice spacings of YSZ [15,16,19]. A calculation showed that epitaxially stretched SrRuO$_3$(110) bottom electrodes should be able to favour the nucleation of (100)-oriented BLT nuclei over that of (118)-oriented nuclei. In view of the negative SrRuO$_3$(110)/YSZ(100) lattice misfit, very thin SrRuO$_3$(110) bottom electrodes should grow in a stretched state. In result of these calculations and observations, we assumed that there should be a strong dependence of the crystallographic orientation of BLT films on the thickness of the underlying SrRuO$_3$ electrode.

Before experimentally studying this influence of the thickness of the SrRuO$_3$ bottom electrode onto the orientation of the BLT film, the optimum growth temperature for SrRuO$_3$ layers was found studying the crystallographic perfection of the layers by XRD [20]. In result, this optimum growth temperature was found to be 775 °C. The result of a subsequent XRD and AFM study of the orientation of BLT films, and of their crystal perfection in terms of the full width of half maximum (FWHM) of $\omega$ rocking curves, all as functions of the thickness $t$ of the underlying SrRuO$_3$ bottom electrode, is shown in Fig. 1. This figure shows AFM topography images (a-d) of

![AFM images](image)

**Figure 1.** (a)-(d) AFM topography images (image size: 5×5 $\mu$m$^2$), and (e) SrRuO$_3$-thickness dependence of $\omega$-FWHM (left scale) of the BLT 200/020 peak, and of $\alpha_{(100)}$ (right scale), for BLT films grown on SrRuO$_3$/YSZ(100) substrates at $T = 765$ °C. The thickness of the SrRuO$_3$ electrode is $t = 10$ nm (a), 18 nm (b), 25 nm (c), and 50 nm (d), respectively.
BLT films grown on SrRuO$_3$ electrode layers having different thicknesses of $t = 10$ nm (a), 18 nm (b), 25 nm (c), and 50 nm (d). Figure 1e shows the SrRuO$_3$-thickness dependence of the $\omega$-FWHM of the BLT 200/020 peak, and of the volume fraction $\alpha_{(100)}$ of the (100) orientation of BLT. (For the definition and determination of $\alpha_{(100)}$, see Eq. 1 below.) The BLT deposition conditions were kept constant, viz. a deposition temperature of 765 °C, a laser fluence of 2.3 J/cm$^2$, a laser repetition rate of 5 Hz, and an oxygen background pressure of 40 Pa.

As a measure of the proportion (volume fraction) of the (100) orientation in the BLT films, the following figure $\alpha_{(100)}$ was defined:

$$\alpha_{(100)} = \left(\frac{I_{(111)}^{(100)}}{I_{(111)}^{(100)} + I_{(111)}^{(118)}}\right) \cdot 100$$

where $\alpha_{(100)}$ is in percent, and $I_{(111)}^{(100)}$ and $I_{(111)}^{(118)}$ are the 111 peak intensities in $\phi$ scans from the (100)- and (118)-oriented parts of the film, respectively. In addition, $\alpha_{(100)}$ could also be visually estimated from the morphology of the grains visible in AFM images of BLT films, because (100)-oriented BLT grains have an equi-axed morphology, whereas (118)-oriented BLT grains are needle-shaped, see [19,20,23]. For example, there are much more needle-shaped (118) grains present in Fig. 1d ($t = 50$ nm; $\alpha_{(100)} = 47\%$, cf. Fig. 1e) than in Fig. 1a ($t = 10$ nm; $\alpha_{(100)} = 78\%$).

As seen in Fig. 1e, the proportion $\alpha_{(100)}$ of the (100)-oriented part of the film increased from 46% to 78% on decreasing the SrRuO$_3$ layer thickness from 50 nm to 10 nm. The FWHM of the BLT 200/020 peak in the $\omega$ scan correspondingly decreased on decreasing the SrRuO$_3$ thickness.

As a result of this study, 10 nm thin SrRuO$_3$ bottom electrodes on 60 nm thick YSZ buffer layers indeed are able to fulfill the role of a promoter of the (100) orientation of BLT films grown on top of them, most probably due to a stretched state of the SrRuO$_3$ layer. However, only 78% of the BLT nuclei were (100)-oriented on 10 nm thick SrRuO$_3$ bottom electrodes, the others still being (118)-oriented. In order to further promote the growth of the (100)-oriented nuclei into an entirely $a$-axis oriented film, and correspondingly to suppress the growth of the (118)-oriented nuclei, the deposition conditions for the BLT films were further optimized with respect to the highest-possible value of $\alpha_{(100)}$.

First, the optimum deposition temperature for BLT was determined by depositing BLT films on YSZ(100) single crystal substrates and on 60 nm thick YSZ(100) buffer layers on Si(100) wafers, in each case covering the YSZ surface with 10 nm-thick SrRuO$_3$ bottom electrodes. The other BLT deposition conditions (laser fluence, laser repetition rate, oxygen background pressure) were the same as in Figure 1. Since we knew from earlier experiments that the optimum growth temperature of BLT films on 50 nm thick SrRuO$_3$ layers was 765 °C [20], BLT films on 10 nm thick SrRuO$_3$ layers were grown in the range of 755 – 770 °C only, with a temperature step of 5 K. As an example, Fig. 2 shows the result of the experiments carried out on YSZ(100) single crystal substrates. Corresponding AFM topography images and curves of $\alpha_{(100)}$ and $\omega$-FWHM are shown, all as a function of the deposition temperature of BLT. From this and similar experiments the conclusion was drawn that the optimum deposition temperature for the growth of (100)-oriented BLT films on stretched, 10 nm thin SrRuO$_3$ bottom electrodes is 765 °C.

In a similar way, the other deposition conditions (laser fluence, laser repetition rate, and oxygen background pressure) were optimized with respect to a high value of $\alpha_{(100)}$. It turned out that the films had to be deposited at high laser fluence, high repetition rate, and high oxygen pressure.
Figure 2. (a)-(d) AFM topography images (image size: 5×5 µm²), and (e) substrate temperature dependence of ω-FWHM (left scale) of the BLT 200/020 peak, and of α_{(100)} (right scale), for BLT films grown on SrRuO₃/YSZ(100) substrates at t = 10 nm. The substrate temperature during deposition of BLT is T = 755 °C (a), 760 °C (b), 765 °C (c), and 767 °C (d), respectively.

As an example, Figure 3 shows the dependence of the surface topography, of α_{(100)} and of the ω-FWHM of the BLT films on the oxygen background pressure.

As a result of the optimization process, the following optimum conditions were found to enable the growth of uniformly a-axis oriented BLT films: Substrate temperature T = 765 °C, laser fluence J = 3.4 J/cm², repetition rate f = 7 Hz, and oxygen background pressure P = 100 Pa.

Figure 3. (a)-(d) AFM topography images (image size: 5×5 µm²), and (e) oxygen background pressure dependence of ω-FWHM (left scale) of the BLT 200/020 peak, and of α_{(100)} (right scale), for BLT films grown on SrRuO₃/YSZ(100) substrates at t = 10 nm, T = 765 °C, J = 3.4 J/cm², and f = 7 Hz. The oxygen background pressure during deposition of BLT is P = 30 (a), 50 (b), 75 (c), and 100 Pa (d), respectively.
The specific roles of these conditions in attaining the required film orientation have been discussed elsewhere [20]. Briefly, the high oxygen pressure necessary to grow \(a\)-axis-oriented BLT films can most likely be explained in terms of effects related to an improved oxygen incorporation into the growing film as a result of increased vapor/ambient oxygen gas collisions, such as an enhanced oxidation of bismuth. As a result the bismuth desorption from the \(a\)-axis-oriented BLT films may be reduced. This may be significant, because the \(a\)-axis-oriented BLT films have the \(\text{Bi}_2\text{O}_2\) layers perpendicular to the film plane, so that the desorption of bismuth could be rather easy at the relatively high substrate temperature used. In addition, the high laser repetition rate will favor suppression of desorption events by a more frequent supply of ablated species. Moreover, most probably the high film growth rate resulting from the high laser repetition rate additionally favors the (100) orientation by a kinetic growth mechanism. Indeed (100)-oriented films showed a significantly larger film thickness than an almost (118)-oriented film for the same number of laser pulses. This effect is probably due to a higher growth rate along the \(a\) axis and/or a reduction of desorption.

**Structure and properties of the \(a\)-axis oriented BLT films**

Figure 4a shows a pole figure of the BLT 117 reflection, recorded from a BLT film of uniform \(a\)-axis orientation, demonstrating the entire (100) orientation of the film: All peaks are at \(\psi \approx 57^\circ\) (\(\psi\) – polar angle), corresponding to the angle \(\angle(100):(117) = 56.9^\circ\). (The peaks marked with asterisks originate from a shoulder of the YSZ (111) peak.) Each set of peaks consists of two sub-sets (of two peaks each), which differ by \(\Delta \phi \approx 20^\circ\) (\(\phi\) – azimuth) indicating four different azimuthal domains. The presence of these growth domains is due to the specific crystallography of the system as explained in the following, also referring to Fig. 4b.

**Figure 4.** (a) Pole figure of an \((a\)-axis oriented BLT film (117 peak of BLT). The center of the circle corresponds to \(\psi = 0^\circ\), the rim to \(\psi = 90^\circ\) (\(\psi\) – polar angle; \(\psi = 90^\circ\) corresponds to the substrate surface being parallel to the plane defined by the incident and reflected x-ray beams.) All the peaks are on \(\psi \approx 57^\circ\). (b) Schematic of the epitaxy relation between the unit cells of (100)-oriented YSZ (“A”) and (110)-oriented \(\text{SrRuO}_3\) (“B”), also showing the angle of \(19.5^\circ\) between the four different azimuthal variants of \(\text{SrRuO}_3\).
As had been shown by us previously, (110)-oriented SrRuO$_3$ bottom electrodes grow on YSZ(100) with four azimuthal domains [15]. This is a consequence of the fact that due to the specific epitaxy relation, the rectangular projection of the SrRuO$_3$ unit cell onto the (110) plane is azimuthally aligned with respect to the square projection of the YSZ(100) unit cell in such a way that the diagonals of the two unit cells are parallel (Figure 4b). Since there are four possibilities to fulfill this condition, four azimuthal SrRuO$_3$ growth domains result as also shown in Fig. 4b. As seen in the figure, the typical angles between different azimuthal growth domains are 19.5° and 90°, as well as (90 – 19.5) = 70.5°.

These four azimuthal domains of the SrRuO$_3$ bottom electrode result in the presence of corresponding azimuthal domains in the $a$-axis oriented BLT films, which are the reason of the sub-sets of peaks observed in pole figures as in Fig. 4a. The detailed analysis shows that the corresponding epitaxy relationship is

\[
\begin{align*}
\text{BLT}(100) \parallel & \text{SrRuO}_3(110) \parallel \text{YSZ}(100) \parallel \text{Si}(100); \\
\text{BLT}[001] \parallel & \text{SrRuO}_3[001], \text{where SrRuO}_3[\overline{1}11] \parallel \text{YSZ(011)} \parallel \text{Si(011)}
\end{align*}
\]

including four azimuthal domains.

TEM investigations confirmed the $a$-axis orientation. High-resolution TEM images (HRTEM images, Fig. 5) are in very good agreement with BLT structure models (superimposed on Fig. 5). Figure 6 shows a plan-view TEM image of three neighboring azimuthal domains. The $c$ axes of these domains are clearly in the plane of the film, but they differ by azimuthal angles of 20°, 70°, and 90°, respectively, in correspondence with the azimuthal differences of the underlying SrRuO$_3$ domains. However, the $a$-axis of all the azimuthal BLT domains being perpendicular to the film plane, all these domains have identical electrical properties along the film normal. As a consequence, these films have a high remanent polarization, as shown below.

![Figure 5](image.png)

**Figure 5.** High-resolution transmission electron micrograph of a cross section of an $a$-axis oriented BLT grain, and superimposed Bi$_4$Ti$_3$O$_{12}$ structure model. The $c$ axis points to the right, the $a$ axis upwards. Viewing direction is along the $b$ axis.
Figure 6. Plan-view HRTEM image of three neighboring azimuthal domains in a uniformly $a$-axis oriented BLT film ($c - c$ axis, lying in the plane of the paper; $P$ – polarization vector, pointing perpendicularly to the plane of the paper.)

Figure 7. $P$–$E$ hysteresis loop of a Pt-BLT(100)-SrRuO$_3$(110) capacitor with a BLT(100) film of 1 µm thickness.
Figure 8. Fatigue endurance of a 1 µm thick BLT film of 99% a-axis-orientation recorded with the AixACCT TF Analyzer 2000. The value of switching polarization $P_{sw} = (P_{max+} - P_{rr-})$ is shown as a function of the number of switching cycles up to a number of $10^9$ cycles, where $P_{max+}$ is the polarization value at positive saturation, and $P_{rr-}$ is the polarization in the negative relaxed remanent state.

Figure 7 represents a ferroelectric polarization-electric field ($P$-$E$) hysteresis loop of a 1 µm thick a-oriented BLT film, recorded at 200 Hz at a maximum applied field of 740 kV/cm, with Pt top electrodes 100 µm in diameter. A remanent polarization of 32 µC/cm² has been attained, which is a new record for bismuth-layered perovskite films on substrates.

Figure 8 shows the result of a provisional fatigue test up to $10^9$ switching cycles. The fatigue experiment has been performed at a reduced testing electric field of 150 kV/cm in order to avoid any danger of breakdown during the long-time experiment. In spite of some fluctuation of the switching polarization within a range of ± 10%, the origin of which is not clear, almost no fatigue has been observed up to $10^9$ switching cycles at a fatigue frequency of 10 kHz.

CONCLUSIONS

Uniformly a-axis oriented Bi$_{3.25}$La$_{0.75}$Ti$_3$O$_{12}$ thin films have been grown on Si(100) substrates buffered with a YSZ layer and electroded with a very thin SrRuO$_3$ bottom layer. The films have a very large remanent polarization in amount of 32 µC/cm² and a suitable fatigue resistance, pointing to the high potential of a-axis oriented Bi$_{3.25}$La$_{0.75}$Ti$_3$O$_{12}$ thin films with respect to memory applications.
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