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Selectable texture in epitaxial ferroelectric BaTiO₃ films integrated with silicon

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Ferroelectric BaTiO₃ films have been epitaxially grown by pulsed laser deposition on buffered Si substrates. We show that BaTiO₃ films texture is selectable by appropriate choice of Si wafer orientation and buffer layers. BaTiO₃ films having (001), (101) or (101)/(100) texture present very flat surface, low current leakage, and sizeable ferroelectric polarization. The films, integrated on silicon platforms, offer opportunities to exploit anisotropic optic and dielectric properties of ferroelectric BaTiO₃.

Introduction

Ferroelectric oxides are strongly anisotropic, and the in-plane and out-of-plane polarization of epitaxial ferroelectric thin films can depend critically on the film orientation. Similarly, piezoelectric and electrooptical coefficients are highly anisotropic. Epitaxial ferroelectric films are usually deposited on (001) oriented cubic (or pseudocubic) substrates. The polar *c*-axis of BaTiO₃ (BTO) or PbZr_xTi_{1-x}O₃ (PZT) films on these substrates is generally aligned either along the out-of-plane direction (named *c*-oriented, or (001)-oriented films) or along an in-plane direction (named *a*-oriented, or (100)-oriented films). Epitaxial growth of tetragonal ferroelectrics with orientation different to (001) or (100) has been much less investigated even though their anisotropic properties offer opportunities for new technologic developments. As example of genuine properties derived from uncommon textures, peculiar patterns of crystal variants and domain walls were observed in PZT(101) films.¹⁻² Typically, (110)-oriented perovskite substrates instead of the usual (001) ones are used to obtain epitaxial PZT(101) films.

Epitaxial ferroelectric oxides on Si(001) are generally (001) or (100) oriented and rarely present different texture.³⁻⁹ Exceptions include (110)-oriented PZT¹⁰ on SrRuO₃/CeO₂/yttria-stabilized zirconia (YSZ)/Si(001), and PbSc_{0.5}Ta_{0.5}O₃ (ref. 11) and BTO¹² films on SrRuO₃/YSZ/Si(001). Integration of high-quality BTO(110) films with silicon is particularly elusive, presenting the films¹² large roughness and their electrical properties remain undisclosed. In contrast, flat BTO(001) epitaxial films with large polarization have been obtained on Si(001) buffered with either LaNiO₃ (LNO)/SrTiO₃ (ref. 3) or LNO/CeO₂/YSZ (ref. 4-6). Aiming to obtain flat epitaxial

BTO(110) films on silicon, we have investigated two routes alternatives to the usual LNO/CeO₂/YSZ buffer layer and the usual Si(001) orientation (Figure 1a, left panel). The first route (Figure 1a, right panel) involves the use of the alternative LNO/CaTiO₃ (CTO)/YSZ buffer layer on Si(001). In the second route (Figure 1a, middle panel) we use the conventional LNO/CeO₂/YSZ buffer but replacing the Si(001) substrate by Si(111). We show that very flat epitaxial BTO films are obtained in both cases, being the films (101) oriented on LNO/CTO/YSZ/Si(001) and presenting coexistence of (101) and (100) out-of-plane oriented epitaxial crystal variants on LNO/CeO₂/YSZ buffered Si(111). The BTO films have low leakage current and are ferroelectric with remnant polarization in the 1.9 – 4.5 μC/cm² range.

Experimental

BTO films (thickness *t*=110 nm) were deposited on LNO (*t*=30 nm)/ CeO₂ (*t*=20 nm)/ YSZ (*t*=60 nm) buffered Si(001) and Si(111), and LNO (*t*=30 nm)/ CTO (*t*=50 nm)/ YSZ (*t*=2.5 nm) buffered Si(001). The samples were prepared by pulsed laser deposition in single processes on as received Si substrates. The first layer, YSZ, reduces the native amorphous SiO_x permitting epitaxial crystallization.¹³ CTO was deposited at 750 °C, 0.02 mbar of molecular oxygen and laser frequency of 5 Hz. The deposition conditions used for the other buffer layers and BTO are reported elsewhere.⁴⁻⁵ Crystal orientation, epitaxial relationships and lattice parameters were determined by X-ray diffraction (XRD) using CuK_α radiation. Topographic images were recorded by atomic force microscopy (AFM). Square Pt contacts (20 nm thick, 60 μm wide) for electrical measurements were deposited *ex-situ* through shadow masks. Ferroelectric polarization loops and leakage current density curves were measured at room temperature using a TFAAnalyser2000 platform (aixACCT Systems) contacting two top Pt-electrodes, with the conducting LNO buffer layer as

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Fig. 1: (a) Sketches of the heterostructures with (001), (101)/(100) and (101) texture of BTO. (b) XRD symmetrical θ - 2θ scans of BTO(001) (top), BTO(101)/(100) (middle) and BTO(101) (bottom). Vertical dashed lines at $2\theta = 22.039^\circ$, 31.498° , 44.856° , and 65.755° mark the positions of 001, 101, 002, and 202 reflections in bulk BTO, respectively. The intensity is in logarithmic scale and the scans are vertically shifted for clarity. (c) Zoom of the diffractograms in the $20 - 50^\circ$ 2θ range. Dashed lines mark the position of 001, 101, and 002 reflections in bulk BTO.

common electrode (two capacitors are measured in series in this configuration).

Results

The XRD specular θ - 2θ scans of all samples are presented in Figure 1b. Vertical dashed lines at $2\theta = 22.039^\circ$, 31.498° , 44.856° , and 65.755° mark the position of the 001, 101, 002, and 202 reflections in bulk BTO, respectively. XRD ϕ -scans around asymmetrical reflections were recorded using a 2D detector to determine the epitaxial relationships in all samples (Fig. 2). The upper scan in Fig. 1b, corresponding to the BTO/LNO/CeO₂/YSZ/Si(001) sample (left sketch in Fig. 1a), shows (001) reflections of the Si substrate and films, without peaks corresponding to other phases or orientations. The BTO 001 reflections (see a zoom in Figure 1c) are at slightly lower angles than in bulk BTO, signaling expanded out-of-plane c -parameter. Figure 2a shows the ϕ -scans of (110) or (220) reflections corresponding to this sample. Each ϕ -scan shows four peaks 90° apart, being the CeO₂ and Si peaks overlapped (see in the lower panel a Gaussian fit for the CeO₂ peak. BTO 110 and LNO 110 peaks shifted 45° respect the other sets of peaks. It confirms⁴ cube-on-cube growth with 45° in-plane

rotation between LaNiO₃ (lattice parameter $a = 3.86 \text{ \AA}$) and CeO₂ ($a = 5.41 \text{ \AA}$).

The BTO/LNO/CeO₂/YSZ/Si(111) sample is sketched in Fig. 1a, middle panel. The XRD specular θ - 2θ scan (Fig. 1b and 1c, middle scans) shows that YSZ is (111) oriented although with presence of minority (001) domains. The 111 reflections of CeO₂ are overlapped with Si 111 ones. LNO and BTO are preferentially (101)-oriented, with minority (100) domains. The formation of (101) and (100) out-of-plane oriented domains of LNO on the CeO₂(111) surface is caused by the large lattice mismatch between both oxides, being the corresponding lattice parameters $3.84 \text{ \AA}$ and $5.41 \text{ \AA}$, respectively. Whereas in the sample on Si(001), LNO(001)/CeO₂(001) texture relationship happens by 45° in-plane rotation (Fig. 2a), a similar lattice matching is not possible on the three-fold symmetry CeO₂(111) surface. The ϕ -scans of this sample are presented in Fig. 2b. The scan around Si 220 reflection displays three high intensity peaks, whereas there are six YSZ 220 reflections indicating the presence of two YSZ crystal in-plane variants, one of them more abundant than the other. These $\Sigma 3$ twinning domains, one rotated 180° in-plane respect the other, are usual in epitaxial films with (111) out-of-plane orientation.¹⁴⁻¹⁷ On the other hand, the observation of six reflections associated with CeO₂(220) planes (see a Gaussian fit in the lower panel),

Fig. 2: XRD ϕ -scans (a) around BTO 110, LNO 110, YSZ 220 and CeO_2 and Si 220 asymmetrical reflections of the BTO(001)/LNO/ CeO_2 /YSZ/Si(001) sample. Lower panel: zoom of the Si and CeO_2 220 reflections. The red curve is a Gaussian fit of the latter. (b) BTO 101 and 002, YSZ 220 and CeO_2 and Si 220 asymmetrical reflections of the BTO(101)/(100)/LNO/ CeO_2 /YSZ/Si(111) sample. Lower panel: zoom of the Si and CeO_2 220 reflections. The red curve is a Gaussian fit of the latter. (c) BTO 111, LNO 200, CTO 200 and Si 220 asymmetrical reflections of the BTO(101)/CTO(110)/YSZ(001)/Si(001) sample. Lower panel: zoom of the Si 220, LNO 200 and CTO 200 reflections. The red curve is a Gaussian fit for the LNO 200 and CTO 200 reflections.

indicates the presence of domains distribution similar to that of the YSZ described earlier. Finally, we confirm by ϕ -scans measurements of BTO asymmetrical reflections (Fig. 2b) that the two domains in BTO, (101) and (100) oriented, are epitaxial. In the case of BTO(101) textured, the ϕ -scans around the BTO(002) asymmetrical reflections show two sets (60° apart) of three peaks corresponding to two BTO crystal variants. On the other hand, in the case of the BTO crystal variant with (100) texture, the asymmetrical BTO 101 reflections show 24 peaks, 15° apart. In this ϕ -scan, two sets of three peaks have higher intensity, which correspond to [010]BTO(100) domains rotated $\pm 15^\circ$ in-plane respect to [11-2]Si(111). The third sample, BTO/LNO/CTO/YSZ/Si(001), is sketched in Fig. 1a, right panel. The XRD θ -2 θ scan (Fig. 1b, lower scan) shows diffraction peaks corresponding to BTO 101, LNO 110 and Si 001 reflections. The lattice parameters of CTO ($a = 3.83 \text{ \AA}$)

and LNO ($a = 3.86 \text{ \AA}$) are very close and their XRD reflections are at the same 2θ positions. The YSZ layer in this sample is 2.5 nm thick, permitting epitaxial crystallization of YSZ(001) on SiO₂/Si(001).^{13,18} Thus, the texture relationship is BTO(101)/LNO(110)/CTO(110)/YSZ(001)/Si(001). The XRD ϕ -scans are shown in Fig. 2c. Narrow peaks corresponding to Si(220) reflections overlap with CTO 200 and LNO 200 reflections (see a Gaussian fit in the lower panel). The ϕ -scan around BTO 111 reflections (Fig. 2c, top panel) shows four broad peaks signaling the presence of in-plane [010]BTO(101) domains around [100]Si(001). This type of domains is usually observed in epitaxial oxide heterostructures with high lattice mismatch.^{11,19,20} Figure 3 shows AFM topographic images, 5 $\mu\text{m} \times 5 \mu\text{m}$ in size (1 $\mu\text{m} \times 1 \mu\text{m}$ in the insets). The BTO(001) film on LNO/ CeO_2 /YSZ/ Si(001) (Fig. 3a) presents small grains a few tens of

Fig. 3: Topographic AFM images ($5\ \mu\text{m} \times 5\ \mu\text{m}$) of the (a) BTO(001)/LNO/CeO₂/YSZ/Si(001), (b) BTO(101)/(100)/LNO/CeO₂/YSZ/Si(111), and (c) BTO(101)/CTO(110)/YSZ(001)/Si(001) samples. The corresponding height ranges are 7, 4 and 7 nm, respectively. Insets: $1\ \mu\text{m} \times 1\ \mu\text{m}$ images, being the corresponding height ranges 5, 4, and 5 nm. Some of the grain boundaries in BTO(101)/CTO(110)/YSZ(001)/Si(001) sample are oriented along [1-10] and [001] directions of BTO (marked with solid red lines in the inset of panel (c)). Lower panels show height profiles along the horizontal lines marked in the corresponding $5\ \mu\text{m} \times 5\ \mu\text{m}$ topographic image.

nanometers wide, locally agglomerated in some small areas a few nm high (see in the lower panel the height profile along the line marked in the topographic image). The overall roughness, root means square (rms) of 0.74 nm, is remarkably low considering the BTO thickness ($t > 100\ \text{nm}$). Additional information about the surface morphology of BTO(001) films on Si(001) is reported elsewhere.^{5,6} The BTO(101)/(100) film LNO/CeO₂/YSZ/Si(111) (Figure 3b) presents similar morphology of small grains, being the roughness very low (rms

= 0.44 nm) and the surface very homogeneous in spite of the coexistence of the two crystalline orientations. The BTO(101) film on LNO(110)/CTO(110)/YSZ(001)/Si(001) (Figure 3c) shows dense morphology of large grains (a few hundred of nm wide), with some grain boundaries (see two examples marked with white dotted lines) oriented along BTO[1-10] and BTO[001] directions. The grains are very flat (see the corresponding height profile) and the overall roughness very low (rms

Fig. 4: (a) Ferroelectric polarization loops, and (b) leakage current density of the BTO(001) film on LNO/CeO₂/YSZ/Si(001), BTO(101)/(100) film on LNO/CeO₂/YSZ/Si(111), and BTO(101) film on CTO(110)/YSZ(001)/Si(001).

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nm). Therefore, the BTO(101) films on Si(001) substrates are extremely flat in comparison to previous reports¹² and present low roughness comparable to state-of-the-art BTO(001) films on Si(001)⁶⁻⁸.

Ferroelectric polarization loops of the BTO(101)/(100)/LNO/CeO₂/YSZ/Si(111) and BTO(001)/LNO/CeO₂/YSZ/Si(001) samples were measured (Figure 4a) by dynamic hysteresis mode,²¹ whereas dielectric leakage current compensation²² was used for the BTO(101)/CTO(110)/YSZ(001)/Si(001) sample due to its higher leakage at high electric field. The (001) film has the largest polarization at high electric field, as expected considering that the polar axis of BTO is along the *c*-axis. Its remnant polarization P_r is 3.2 $\mu\text{C}/\text{cm}^2$, whereas in the BTO(101)/(100), and BTO(101) films P_r is 1.9 and 4.5 $\mu\text{C}/\text{cm}^2$, respectively. Figure 4b shows leakage curves measured at room temperature. The leakage of the BTO(001) film on LNO/CeO₂/YSZ/Si(001) (black squares) is very low: 7×10^{-8} A/cm² and 2×10^{-3} A/cm² at 45 and 450 kV/cm, respectively. The leakage of the BTO(101)/(100) film on LNO/CeO₂/YSZ/Si(111) on Si(111) is higher at low field (3×10^{-7} A/cm² at 45 kV/cm), whereas in the BTO(101) film on CTO(110)/YSZ(001)/Si(001) is similar to the BTO(001) sample (8×10^{-8} A/cm² at 45 kV/cm). However, the leakage of this film increases sharp with field, while the increase of the BTO(101)/(100) is smaller.

Conclusions

In summary, suitable selection of buffer layers and silicon wafer orientation permits controlling the crystallographic orientation in epitaxial BTO films. BTO(001), BTO(101) and BTO(101)/(100) textures are achieved on LNO/CeO₂/YSZ/Si(001), LNO/CTO/YSZ/Si(001), and LNO/CeO₂/YSZ/Si(111), respectively. BTO(001) films are fully epitaxial, whereas the other BTO films present coexistence of crystal domains. All the films, irrespectively of their orientation, are extremely flat with low rms roughness (in the 0.4 – 0.8 nm range), present low leakage (in the 7×10^{-8} – 3×10^{-7} A/cm² range at 45 kV/cm) and sizeable remnant polarization in the 1.9 – 4.5 $\mu\text{C}/\text{cm}^2$ range. The films can pave the way towards devices taking benefit of the anisotropic properties of ferroelectric BaTiO₃.

Conflicts of interest

There are no conflicts to declare.

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