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# Controllable growth of ultrathin BiFeO<sub>3</sub> from finger-like nanostripes to atomically flat films

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## Abstract

BiFeO<sub>3</sub> (BFO) ultrathin films with nominal thicknesses from 2 to 12 nm were grown with a  $SrRuO_3$  (SRO) buffer layer on TiO<sub>2</sub>-terminated (001)  $SrTiO_3$  (STO) substrates using pulsed laser deposition. The surface morphologies and domain configurations of the thin films were investigated using atomic force microscopy and piezoelectric force microscopy. Periodical one-dimensional finger-like nanostripes of BFO on the SRO covered STO substrates were observed. With increasing thickness, the BFO ultrathin films develop from the finger-like nanostripes to an atomically flat surface. The formation of the finger-like nanostructures of BFO is related to the atomic step or terrace structure of the substrate. The BFO nanostripes and the atomically flat thin films are ascribed to the chemical terminations at the surface of the SRO layer. These results indicate that the surface morphologies and the domain configurations of BFO ultrathin films can be artificially designed by using substrates with optimized terrace structures and chemical termination, and these films are potentially useful in multifunctional nanoelectronic devices.

Keywords: multiferroic BiFeO<sub>3</sub>, finger-like nanostripes, atomically flat ultrathin films, surface morphology, domain configuration, ferroelectricity, patterned nanostructures

(Some figures may appear in colour only in the online journal)

# 1. Introduction

Multiferroic materials, which exhibit simultaneously electric and magnetic orders, provide many possible application [1– 3]. As one of the most well-known multiferroic materials, BiFeO<sub>3</sub> (BFO) has attracted great interest because of its high remanant polarization, large piezoelectric response, high Curie temperature (~1100 K), and high Neel temperature (~643 K) [4, 5]. BFO thin films from several nanometers to hundreds of nanometers in size have been widely studied for their interesting physics and potential device applications [6– 9]. BFO films possess rhombohedral distortion along one of the four (111) crystallographic directions of the pseudocubic perovskite unit cell, thus eight possible polarization variants may form in the films, leading to complex domain patterns. The physical properties, such as crystallinity and microstructure, of the films are significantly dependent on their growth conditions and the film thickness. In particular, the surface step or terrace structures of substrates and lattice mismatch have a large influence on the initial growth mode. Therefore, an understanding of the growth mode at an atomic level is important to improve the crystal quality and physical performance of the films. Studies have shown that BFO films show complicated domain structures, and the final domain structure might be influenced crucially by the terraces or steps on the substrate [10]. BFO films grown on vicinal substrates can assist in the engineering of ferroelectric domain structure [11, 12]. Yu *et al* have demonstrated that the as-grown

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Figure 1. AFM images of a TiO<sub>2</sub>-terminated STO substrate (a) and a 10 nm thick SRO thin film on the STO substrate (b).

polarization direction of BFO films can be determined by the interfacial chemical termination and its fine level control of the interface electrostatic potential [13]. Therefore, by choosing the terrace structure and chemical termination of substrates and the deposition conditions, the morphologies and domain structures of BFO thin films can be partially modulated.

BFO exhibits collective responses to the electric, magnetic, and stress fields, and the coupling between two order parameters provides an addition degree of freedom in device design. In particular, ultrathin BFO films have the potential for use in multiferroic tunneling junctions as tunneling barriers, which may lead to multistate memory devices [14]. The growth of patterned structures from surfaces with nanometersized periodicities is becoming of increasing scientific and technological interest in the field of materials nano-engineering. Patterned nanostructures may play a key role in the development of high-density electronic devices. Sánchez et al have reported finger-like nanostripes of conductive SrRuO<sub>3</sub> (SRO) ultrathin films on SrTiO<sub>3</sub> (STO) substrates [15–17]. By controlling the substrate terrace structure, surface termination, and selected deposition conditions, epitaxial SRO films on STO substrate can be grown into geometric shapes of either one-dimensional stripes [16, 17] or a two-dimensional layer [18, 19]. However, until now, there has been no research on ultrathin BFO nanostripes. In this work, we report the growth of ultrathin BFO films from finger-like nanostripes to atomically flat thin films and the effect of the morphology evolution on their ferroelectric properties and domain configurations.

#### 2. Experimental details

BFO ultrathin films with a 10 nm thick SRO bottom layer were grown on (001) STO substrates using pulsed laser deposition. A XeCl 308 nm excimer laser was used with an energy density of around 1.5 J cm<sup>-2</sup> and a repetition rate of 2 Hz. The nominal thicknesses of the BFO ultrathin films are 2, 4, 8, and 12 nm, which were controlled by varying the number of laser ablation pulses. During the deposition of both the BFO and SRO layers, the substrate temperature was kept around 610 °C, monitored by an infrared pyrometer, and the oxygen pressure in the chamber was 10 Pa. After the deposition, the samples were annealed under 10 Pa oxygen pressure at the deposition temperature for 20 min, and then cooled down to room temperature. Before fabricating the films, commercially available vicinal (001) STO substrates, with miscut angles of less than  $0.3^{\circ}$ , were cleaned with organic solvents and deionized water in an ultrasonic bath, and were then etched in buffered NH<sub>4</sub>F-HF solution to remove the SrO atomic layer at the STO surface. The etched samples were annealed in flowing oxygen at 950 °C to obtain an atomically flat TiO<sub>2</sub>-terminated surface. Atomic force microscopy (AFM) measurements on the obtained TiO<sub>2</sub>-terminated STO substrates show clear and regular step or terrace structures. The crystal structures of the thin films were revealed using x-ray diffraction (XRD; Rigaku) measurements. Piezoresponse force microscopy (PFM; Asylum Research MFP-3D) was used to measure the surface topographies, domain configurations, and local electric properties of the BFO ultrathin films.

### 3. Results and discussion

Figure 1(a) shows the surface of a treated STO substrate, where the steps are of single unit cell height and the terrace width is around 250 nm. The terrace width is consistent with a miscut angle about 0.1° for the STO substrates. To determine the surface structure of the SRO bottom layer, a 10 nm thick SRO film was grown on the STO substrate. Figure 1(b) shows the surface morphology of the SRO layer, indicating that the SRO film has an atomically flat surface with a step and terrace structure. The periodicity of the terraces or steps on the SRO surface is consistent with that on the STO substrate, but the step edges of the SRO film are much rougher than those of the STO substrate. This indicates that the SRO films grown in our conditions show an atomically flat surface and the step and terrace structure on STO substrates can be formed correspondingly on SRO films.

Figure 2(a) shows the XRD patterns of the BFO samples; XRD results for the SRO film on STO, and a STO substrate are also shown for comparison. For the BFO samples, only (001) diffraction peaks of BFO and SRO can be detected, which suggests epitaxial growth of both the BFO and SRO



**Figure 2.** (a) XRD patterns for the BFO ultrathin films with thicknesses of 12, 8, 4, and 2 nm (from top to bottom), on SRO/STO and STO substrates. The inset shows the peak shift of BFO (003) peaks with thickness. (b)  $\phi$  scans of (104) reflection of BFO and SRO thin films. (c) Rocking curves of (002) reflection of BFO and SRO thin films.

layers with no signature of impurities. As expected, the variation of the BFO film thickness causes a systematic change in peak intensity. Moreover, it can be seen that the BFO (003) peaks shift slightly to a higher  $2\theta$  angle with increasing thickness, as shown in the inset of figure 2(a). The out-ofplane lattice constant of the BFO films calculated from the (002) diffraction peaks is about 0.406 nm, which is much larger than the value of 0.396 nm for BFO bulk. This is attributed to the compressive in-plane strain from the lattice mismatch between the BFO and the SRO bottom layer on substrate. The compressive in-plane isotropic strain results in an elongation in the out-of-plane direction of BFO unit cells. It has been reported that for the BFO films thinner than 30 nm the lattice parameters reach a maximum value, which means a fully epitaxial and strained state [7]. With increasing thickness, this strain decreases gradually and the (001) diffraction peaks shift toward a higher  $2\theta$  angle. In our case, the BFO ultrathin films should be fully strained in the thickness range from 2 to 12 nm. The slight shift of peak position with thickness indicates the decrease of the out-of-plane lattice parameters and the relaxation of the compressive in-plane strain with increasing thickness. The strain modification with thickness may also contribute to the variation of domain configuration and coercive field as discussed later.

The in-plane texture of the films was investigated using a  $\phi$  scan of the (104) plane of the films. Figure 2(b) shows  $\phi$  scan results for the 12, 8, and 4 nm BFO films, and the 10 nm SRO thin films. Peaks with four-fold symmetry, 90° apart with high intensity, were observed for the BFO and SRO films, indicating in-plane epitaxial growth of the films. Figure 2(c) shows the rocking curves ( $\omega$  scan) of the (002) diffraction peak for the BFO and SRO films. The full width at half maximum values are about 0.1° for the BFO thin films and 0.08° for the SRO film, which indicates that the films are well crystallized.

Surface morphology scans of the samples with an area of  $2 \mu m \times 2 \mu m$  are shown in figure 3. The AFM images reveal the morphology evolution of BFO films with increasing thickness. On the surface of the 2 nm BFO sample, periodical one-dimensional finger-like nanostripes can distinctly be observed. These finger-like stripes are different from the other common islands or protrusions observed on the surface of thicker BFO films [11]. The one-dimensional stripes are separated by narrow trenches and show a periodicity with an average width of over 100 nm. The finger-like stripes with a thickness around several nanometers are parallel to the step edges and show the same periodicity as the steps or terraces on the used substrate.

As mentioned above, by controlling the deposition conditions, epitaxial SRO films on STO substrates can be grown into geometric shapes of either one-dimensional stripes [16, 17] or a two-dimensional layer [18, 19]. In our deposition conditions, the obtained SRO bottom layer shows an atomically flat surface with corresponding steps and terraces on the TiO<sub>2</sub>-terminated STO, as shown in figure 1. However, it is surprising that one-dimensional nanostripes of BFO can be formed subsequently on the atomically flat SRO. In general, the morphology of a material grown on a substrate may depend on the balance between the free surface energies of the substrate, over-layer, and interface. In epitaxial growth, atomic steps on the surface are of crucial importance since they can trigger kinetic instabilities producing coarsened final surfaces. The formation of the long finger-like nanostructure may be due to one-dimensional growth from the preferential nucleation at step edges in the early growth stage [16]. In our case, the growth of the BFO nanostripes can be attributed to the preferential nucleation of BFO at the step edge sites on the bottom SRO layer. This process may include the growth of two- or three-dimensional BFO islands around the step edges of SRO at low coverage and then their consequent conversion into one-dimensional BFO stripes at higher coverage. Therefore, the step or terrace structure on the STO substrate would be a key factor for the formation of one-dimensional nanostripes of BFO. Moreover, the compressive stress in the BFO films due to the lattice mismatch, as well as other deposition conditions, such as substrate temperature, oxygen



**Figure 3.** Morphology images obtained using AFM of the surface of the BFO ultrathin films with nominal thicknesses of (a) 2, (b) 4, (c) 8, and (d) 12 nm. The height profile perpendicular to the finger-like structure is shown at the top of (a).

pressure, and growth rate, may also have and influence on the one-dimensional growth of the BFO nanostripes.

With further deposition, BFO might be deposited on the stripes and in the trenches, while the adatom diffusion between the adjacent fingers gradually leads to coalescence. Therefore, the trenches become narrow and the stripes are partially coalesced in the 4 nm thick film, while short trenches or holes still exist. After that, a continuous film formed gradually in a fully coalesced sample and, strikingly, the 8 nm thick film shows an atomically flat surface with indistinct steps, which indicates a two-dimensional growth mode in this stage. The 12 nm thick BFO film still has a very flat surface, but starts to show signs of three-dimensional growth. The root mean square roughnesses of this series of BFO ultrathin films are 3.7, 1.1, 0.2, and 0.3 nm, respectively, for the 2, 4, 8, and 12 nm samples. This indicates that the surface roughness of the ultrathin BFO films decreases with increasing thickness. Note that the surface roughness for the 10 nm SRO film on STO is about 0.1 nm, which is much better than that for the BFO thin films. It should be mentioned here that the roughness for the 2 nm BFO films is larger than its nominal thickness. In fact, as shown in the top of figure 3(a), the height profile for the 2 nm BFO sample indicates that the thickness of the finger-like stripes is larger than 2 nm and also that the trenches between the fingers are deeper than 2 nm. Therefore the larger roughness for the 2 nm BFO films is reasonable due to the finger-like surface morphology.

Figures 4(a)-(d) show the evolution of ferroelectric domain configurations with film thickness, recorded through the out-of plane PFM phase image, and figures 4(e)-(h) show the corresponding amplitude mappings. The violet and yellow contrasts in the PFM phase images indicate polarization components pointing down or up, while the black and white contrasts stand for the corresponding amplitude to the inverse piezoelectric response. For the 2 nm thick BFO sample, as shown in figure 4(a), the PFM phase image shows stripe domains corresponding to the finger-like nanostripes on its surface morphology, where the finger-like nanostripes exhibit down polarization and the narrow trenches show up polarization. The as-grown polarization state of BFO is usually determined by the chemical termination of the bottom layer, and BFO grown on SrO terminated SRO would be in the down-polarization state [13]. For SRO thin film grown on TiO<sub>2</sub> terminated STO substrates, a self-organized conversion of the terminating atomic layer from RuO<sub>2</sub> to SrO would happen due to the high volatility of RuO<sub>2</sub> [19]. Therefore, the BFO finger-like nanostripes grown in the early stage show down polarization on the SrO termination of SRO, but the uppolarization state formed in the trenches may be from the possible aggregation of volatile RuO<sub>2</sub> at the narrow trenches



**Figure 4.** (a)–(d) Out-of-plane PFM phase images and (e)–(h) amplitude images for the BFO samples with thicknesses of 2, 4, 8, and 12 nm, respectively.

during an earlier growth stage. With increasing thickness, the up-polarization domains from the trenches grew faster and eventually the up and down domains developed into a random distribution state for the 12 nm thick sample. Usually, the PFM amplitude is comparable for the up and down oriented domains and is small only at the domain boundaries, which can be observed roughly in figures 4(g) and (h) for the amplitude mappings of the 8 and 12 nm samples. However, for the 2 and 4 nm samples, amplitude behavior at domain boundaries cannot be observed in figures 4(e) and (f), which can be ascribed to the thickness difference of BFO on the two sides of a domain boundary due to the existence of trenches or holes.



**Figure 5.** Local piezoresponse phase hysteresis loops and amplitude loops for (a) the 2 nm and (b) the 8 nm BFO samples.

To confirm the ferroelectric nature of these ultrathin BFO films, the local ferroelectric properties of the samples have been investigated using PFM measurements. A local piezo-response phase loop and amplitude loop were obtained for all the four samples. Figures 5(a) and (b) show the phase–voltage loop and amplitude curve for the 2 nm sample with finger-like nanostripes and for the 8 nm samples with an atomically flat surface, respectively. The phase–voltage loop and amplitude curve for the 2 nm sample were taken on the finger-like nanostripes. The observed phase loops for the two samples show almost 180° phase change, and the coercive field

(voltage divided by thickness) decreases with increasing thickness. The phase hysteresis loop with a phase change of 180° is regarded as an evidence of ferroelectric polarization switching. The butterfly shape of the amplitude-voltage curve also indicates that polarization switching occurred. Therefore, these results reveal that both the 2 nm finger-like nanostripes and the atomically flat ultrathin films show good ferroelectricity. In addition, the longitudinal piezoelectric coefficient  $d_{33}$  of our BFO films calculated from the out-of-plane amplitude is about 15 pm  $V^{-1}$ , which is in agreement with reported data [6]. The measured coercive field for the ultrathin films is much larger than that for the films with thickness greater than 100 nm. The compressive in-plane strain would be a key factor for the observed larger coercive field in the ultrathin BFO films. With increasing thickness, the compressive strain in BFO decreases, and therefore the measured coercive filed decreases. Moreover, the intrinsic size effects and the electrode influences may also contribute to the coercive field.

Furthermore, figure 6(a) shows a well-defined PFM image of a  $3 \times 3 \ \mu m^2$  area of the 8 nm BFO film surface after poling with alternative external DC bias. Here,  $-6 \ V$  was applied to a  $2 \times 2 \ \mu m^2$  area followed by  $+6 \ V$  applied to a  $1 \times 1 \ \mu m^2$  center area. The dark violet area is downward polarized and the yellow area is upward polarized. The change in contrast between the two regions shows the occurrence of ferroelectric switching. Figure 6(b) shows the corresponding amplitude image, where the amplitude value for electrically poled domains is enhanced equally for up and down polarization, and the amplitude at the domain wall, i.e. the boundary between the electrically poled domains in opposite orientations, is clearly small.

The morphology evolution with thickness would also have an effect on the magnetic performance of the films. BFO has G-type antiferromagnetism with a spiral spin structure with a period of 62 nm, which subdues net magnetization in bulk BFO. However, the magnetization in nanostructured BFO increases monotonically with a decrease in size [20]. An enhancement of the ferromagnetism in small particles or thin films is usually considered in the context of the suppression of the antiferromagnetic spin cycloid. Therefore, in our case, the ultrathin BFO films show weak



**Figure 6.** Out-of-plane PFM phase image of (a) the 8 nm BFO sample using PFM with alternating +6 V and -6 V DC bias, and the corresponding amplitude image (b).

ferromagnetic properties and the thickness or morphology evolution should have an influence on their magnetic properties. This will be discussed further in the future with more detailed experimental research.

# 4. Conclusion

In conclusion, periodical one-dimensional finger-like BFO nanostripes and atomically flat BFO ultrathin films have been grown successfully on SRO covered TiO<sub>2</sub>-terminated STO substrates. The one-dimensional finger-like stripes show the same periodicity as the terraces or steps on the substrate. The key factor for the formation of BFO nanostripes is the step or terrace structure on the substrate. Measurements of the ferroelectric domain configuration and switching behavior revealed that the BFO finger-like nanostripes and the ultrathin films show good ferroelectricity. The as-grown domain orientations of the SRO layer. These results suggest that the BFO nanostructure and atomically flat ultrathin films can be artificially designed and fabricated for potential applications in nanoelectronic devices.

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