Ferroelectric domain structures of epitaxial (001) BiFeO₃ thin films

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Ferroelectric domain structures of epitaxial BiFeO₃ thin films on miscut (001) SrTiO₃ substrates have been studied by transmission electron microscopy. BiFeO₃ on 0.8° miscut substrates are composed of both 109° and 71° domains; in contrast, only 71° stripe domains are observed in BiFeO₃ on 4° miscut (001) SrTiO₃ substrates. The domain width in BiFeO₃ on 4° miscut substrates increases as film thickness increases due to a reduction in domain wall energy. The domain configurations of BiFeO₃ thin films affect their ferroelectric switching behavior due to the pinning at the junctions between 109° and 71° domain walls. © 2007 American Institute of Physics.

Multiferroics, which have ferroelectric and ferromagnetic/antiferromagnetic properties simultaneously, have attracted broad interest due to their potential application for novel magnetoelectric devices and for exploring fundamental science in the coupling mechanism between electronic and magnetic order parameters. BiFeO₃ is such a material: ferroelectric with its Curie temperature at 1043 K and G-type antiferromagnetic with its Néel temperature at 655 K. Recently, it has been demonstrated that epitaxial BiFeO₃ thin films have high remanent polarization beyond 0.17 nm.

In this letter, we report the ferroelectric domain structure of epitaxial BiFeO₃ thin films studied systematically by transmission electron microscopy (TEM). Compared to other microscopy techniques, TEM can be used to determine the domain structure unambiguously and to study their interaction with other defects (such as dislocations or cracks). As reported previously, miscut SrTiO₃ substrates have been used for the growth of single domain films of metallic oxide SrRuO₃ films, which promote the growth of high quality epitaxial ferroelectric thin films. We have also studied the influence of miscut angle on the ferroelastic domain structures of ferroelectric BiFeO₃ thin films.

BiFeO₃ thin films with several thicknesses between 200 and 1000 nm were deposited by high-rate off-axis sputtering on 0.8° and 4° miscut (001) SrTiO₃ substrates with 100 nm SrRuO₃ bottom electrodes. The substrate was miscut along the [001] direction. The details of the growth conditions have been given elsewhere. The cross-sectional slices for TEM studies were obtained by cutting the BiFeO₃/SrRuO₃/SrTiO₃ sample parallel to the miscut direction so that the atomic steps on the miscut substrate run along the electron beam direction. TEM studies were carried out on a Philips CM12 operated at 120 kV with a high-angle (±60°) double-tilt holder and on a JEOL 3011 ultrahigh resolution TEM operated at 300 kV with a point-to-point resolution of 0.17 nm.

Figure 1(a) shows a representative dark field cross-sectional TEM image for a 600 nm BiFeO₃/100 nm SrRuO₃ film on a 0.8° miscut (001) SrTiO₃ substrate. It can be seen that there are many fringes along the {101}ₚ (in this letter subscript P represents pseudocubic setting) and {100}ₚ planes of the BiFeO₃ thin films. The selected area electron diffraction (SAED) patterns from two different areas, indicated by circles in Fig. 1(a), are shown in Figs. 1(b) and 1(c). The diffraction pattern in Fig. 1(b), from the region including the {100}ₚ-type fringes, shows the clear splitting on high order reflection spots along the [100] direction, indicated by arrows. This reveals that the {100}ₚ type of fringes are 109° domain walls, which is consistent with previous work for rhombohedral ferroelectric thin films grown on (001) cubic perovskite substrates (such as SrTiO₃). On the contrary, diffraction spots in Fig. 1(c) from the region including the {101}ₚ-type fringes are clearly elongated along the [101]ₚ direction, also indicated by arrows. The corresponding fringes are determined to be 71° ferroelectric domain walls. In addition, Fig. 1(a) shows that the population of {101}ₚ-type domain walls is higher than that of {100}ₚ-type domain walls. Similar phenomena have been observed in rhombohedral lead zirconate titanate bulk materials.

High resolution TEM images in Fig. 2 show the atomic structures of 71° and 109° domain walls in the same specimen. It is evident that the structural width (defined by the contrast change in image) of the 71° domain wall is much smaller than that of the 109° domain wall. This is possible due to the lower energy of 71° domain walls compared with that of 109° domain walls, as discussed below. Phenomenological Landau-Ginzburg free energy calculations show that the {100}ₚ-type domain surface energy is three times that of the {101}ₚ-type twin domain in bulk ferroelectric materials, and are therefore less likely to occur. This conclusion can also possibly be applied to ferroelectric thin films because the x-ray diffraction and electron diffraction results described above show that the BiFeO₃ thin films studied in this work...
have been fully relaxed via the formation of domains and misfit dislocations.\(^5\)

In comparison with films grown on 0.8° (001) SrTiO\(_3\) substrates, the domain structure of BiFeO\(_3\) with the different thicknesses grown on 4° miscut SrTiO\(_3\) were also studied. Figure 3(a) shows a representative TEM image of the 200 nm BiFeO\(_3\)/100 nm SrRuO\(_3\) film grown on 4° miscut SrTiO\(_3\) substrate. Fringes parallel to [101]\(_p\) direction can be seen in these BiFeO\(_3\) thin films. In accordance with the previous discussion, these fringes are 71° domain walls. A more interesting point is that there are no 109° domain walls in this sample. Similar results were obtained on 600 nm BiFeO\(_3\)/100 nm SrRuO\(_3\) heterostructure grown on 4° miscut SrTiO\(_3\) substrate, which is shown in Fig. 3(b). It is apparent that the \{101\}_\(p\) type 71° domain walls in BiFeO\(_3\) grown on 4° miscut SrTiO\(_3\) (Fig. 4) are distributed much more uniformly in comparison with the films grown on 0.8° (001) SrTiO\(_3\) substrates. Plane-view TEM observations (not shown here) of the same films show that the 71° stripe domains are oriented perpendicular to the miscut direction, [100]_\(p\), in films grown on 4° miscut SrTiO\(_3\), but run along both the [100]_\(p\) and [010]_\(p\) directions in films grown on exact (001) SrTiO\(_3\). This explains why no domain walls are seen in some regions of cross-sectional specimen. These results agree well with the in-plane PFM observations of the same films, as studied in this work.\(^5\)

These studies imply that the atomic steps induced by the miscut of SrTiO\(_3\) provide a preferred location for the nucleation and growth of 71° domains. It has been suggested that the nucleation of single domains on miscut substrates is due to either surface energy minimization or control of growth parameters to facilitate the step-flow growth from atomic steps, terraces, and kinks on the surface of vicinal substrate.\(^14,15\)

The growth of domains in BiFeO\(_3\) thin films involves the motion of domain walls, which are oriented along the \{101\}_\(p\) planes, in parallel with the [100] or [010] directions of SrTiO\(_3\). The substrate surface steps oriented perpendicularly to the miscut direction [100] induced by miscut can play a role to pin the domain walls and limit the growth of domains in the direction perpendicular to the steps, thus resulting in the one-dimensional array of stripe domains observed.

The relationship between domain width and thin film thickness has been studied by phenomenological Landau-Ginzburg-Devonshire theory and mechanical defect theory.\(^12,16,17\) If the thickness of thin films is much larger than the domain width, the dependence of domain width \(l\) at equilibrium on the thin film thickness \(h\) can be written as

\[
\ell_{\text{thick}} = 2^{3/4} \left( \frac{\pi}{\ln 2} \right)^{1/2} \sqrt{\frac{\sigma h}{E \omega^2}},
\]

where \(E\) represents Young’s modulus, \(\sigma\) the domain energy, and \(\omega\) the rhombohedral distortion.\(^12\) The same scaling law is also kept for domain structure in ferroelectric thin films with tetragonal structure.\(^12\) To test this relationship, two other BiFeO\(_3\) thin films with thicknesses of 450 nm and 1 \(\mu\)m grown on 4° miscut SrTiO\(_3\) substrates were studied. The relationship between domain width and film thicknesses is shown in Fig. 4. The solid line is the fitted result by means of Eq. (1), which agrees well with the experimental values measured in TEM images. The fitting of experimental results in Eq. (1) gives the 71° domain wall energy of 9.2 \(\times 10^{-2}\) J/m\(^2\). In this calculation, Young’s modulus is estimated to be 100 GPa, a typical value for perovskite oxides.\(^12\) The calculated domain energy of BiFeO\(_3\) thin films is of the same order as other oxides with perovskite structure (~\(10^{-2}\) J/m\(^2\)).\(^12\)
Different domain structures observed in BiFeO$_3$ thin films grown on 0.8° and 4° miscut (001) SrTiO$_3$ substrates result in different ferroelectric properties. The saturated spontaneous polarization of 600 nm BiFeO$_3$ grown on 0.8° and 4° miscut (001) SrTiO$_3$ substrates are 52.3 and 57.9 $\mu$C/cm$^2$, respectively. TEM studies show that the BiFeO$_3$ thin films grown on 0.8° (001) SrTiO$_3$ substrate are composed of 71° and 109° domains, while there is only 71° domain in BiFeO$_3$ on 4° miscut SrTiO$_3$. As a result, there exist a number of line defects at the junction between 70° and 109° domain walls in films grown on exact (001) SrTiO$_3$ substrates. The arrangement of atoms along these defects is highly disordered, thus domain walls can be pinned by these line defects. This may inhibit full polarization when the external electric field is applied to thin films. Therefore, the multidomain structure in BiFeO$_3$ thin films grown on 0.8° SrTiO$_3$ substrates possibly leads to a lower saturated spontaneous polarization, compared with BiFeO$_3$ thin film grown on 4° miscut SrTiO$_3$.

In conclusion, the domain structures of different thicknesses of BiFeO$_3$ thin films with 100 nm SrRuO$_3$ buffer layers grown on 0.8° and 4° miscut (001) SrTiO$_3$ substrates were systematically studied by transmission electron microscopy. BiFeO$_3$ thin films grown on 0.8° miscut (001) SrTiO$_3$ substrates contained both 71° and 109° domains whereas films grown on 4° miscut (001) substrates contained only 71° domains, which are oriented perpendicular to the miscut direction. The formation of 71° stripe domain arrays is caused by the domain wall pinning at the substrate surface steps induced by miscut. It was also found that the domain width in BiFeO$_3$ thin films grown on 4° miscut (001) substrates increases as film thickness increases due to a reduction in domain wall energy. The crossover of domain walls of different types limits the domain switching under applied field.

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