Detwinning Monoclinic Phase BiMnO$_3$ Thin Film

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BiMnO$_3$ has been a promising candidate as a magnetoelectric multiferroic while there have been many controversial reports on its ferroelectricity. The detailed analysis of its film growth, especially the growth of thin film having monoclinic symmetry has not been reported. We studied the effect of miscut angle, the substrate surface, and film thickness on the symmetry of BiMnO$_3$ thin film. A flat SrTiO$_3$ (110) substrate resulted in a thin film with three domains of BiMnO$_3$ and 1 degree miscut in the SrTiO$_3$ (110) substrate resulted in dominant domain preference in the BiMnO$_3$ thin film. The larger miscut resulted in a nearly perfect detwinned BiMnO$_3$ film with a monoclinic phase. This strong power of domain selection due to the step edge of the substrate was efficient even for the thicker film which showed a rather relaxed growth behavior along the SrTiO$_3$ [1-10] direction.

Keywords : BiMnO$_3$, detwinning, monoclinic, symmetry lowered substrate surface, miscut

1. Introduction

Perovskite metal oxides, ABO$_3$ have a rich variety of physical properties spanning from resistance switching memory, ferromagneticity, ferroelectricity, and colossal magnetoresistance, and high-temperature superconductivity [1-7]. In order to utilize and/or merge these wide functionalities into real devices, it is usually necessary to prepare thin films of these materials.

The strong epitaxial strain during the growth of a metal oxide thin film on top of a single crystalline oxide substrate has the very important merit of easy stabilization of single crystalline oxide film. However, the epi-stabilization sometimes changes the symmetry of the oxide thin film, which often dramatically changes the physical properties. Cubic (111) substrates with a hexagonal in-plane symmetry have been used to epitaxially deposit hexagonal-phased RMnO$_3$, R=Tb, Gd, Dy, with large enhancements in the ferroic properties, whereas these materials have an orthorhombic structure in their bulk state [8, 9].

BiMnO$_3$ (BMO) has a monoclinic structure with $a = 9.533$ Å, $b = 5.606$ Å, $c = 9.854$ Å and $\beta = 110.667°$ [10]. BiMnO$_3$ was expected to have a huge value of polarization in a film with enough compressive or tensile strain

[11]. However, the existence of ferroelectricity in BiMnO$_3$ has not been achieved with a consensus because the symmetry of the grown films was quite different from that of the bulk BMO. The ferroelectricity in *intrinsic* BiMnO$_3$ could be investigated in a thin film which has a single domain and a similar symmetry to that of bulk BiMnO$_3$, i.e., monoclinic symmetry with minimum strain. But the stabilization of monoclinic BMO thin film has not been reported by other groups [14].

To provide more control during the thin film growth, epi-stabilization has been incorporated with a novel approach such as a miscut substrate. Q. Gan *et al*. tried to use a miscut STO (001) substrate to stabilize the SrRuO$_3$ thin film with twins [4]. H.W. Jang *et al*. extended this method to attack subtle domain problems for many interesting functional oxide materials like BiFeO$_3$. *They used a miscut STO (001) substrate to reduce *four* BFO domains on a non-miscut STO (001) substrate to *two* domains [12]. They also insisted that "*Such a complex domain structure can deteriorate the ferroelectric response of the system by external electric field*." Our group reported the use of a miscut STO (001) substrate to control domain and crystallinity in CaHfO$_3$ which is a candidate for the high-k dielectrics [13].

In this report, we have studied in detail the effect of the miscut angle and the film thickness on the symmetry of BiMnO$_3$ thin film. A flat SrTiO$_3$ (110) substrate resulted in a thin film with three domains of BiMnO$_3$ and 1 degree

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miscut in the SrTiO$_3$ (110) substrate resulted in dominant domain preference in the BiMnO$_3$ thin film. The larger miscut resulted in a nearly perfect detwinned BiMnO$_3$ film with a monoclinic phase. This strong power of domain selection due to the step edge of the substrate was even efficient for very thick film although thick BMO films showed a relaxed growth behavior along STO [1-10] direction.

2. Experimental

We grew thin films of BiMnO$_3$ on a SrTiO$_3$ (STO) (110) substrates with miscut angles (0.2 and 1.0 degree) using a pulsed laser deposition method [10]. The details and significance of getting the stoichiometric BMO thin film can be found in our previous report [10]. The thickness was estimated to be, $t = 80$-200 nm, using a field emission scanning electron microscope [FESEM]. We used high-resolution x-ray diffraction to study the crystal structure of the BiMnO$_3$ films.

3. Results and Discussion

Figure 1 shows the θ–2θ patterns of a BMO thin film grown on the top of a nominally flat STO (110) substrate (miscut angle ~0.2 degree). The BMO reflection peaks are clearly visible at the left of the STO (110) substrate peaks. We could not find peaks other than those related to BMO in this range. The x-ray rocking curve of the BMO peak shown in Fig. 1(b) exhibited very narrow peak with FWHM as small as 0.051 degree. The typical interpretation for this narrow rocking curve is that the c-axis crystallinity is very good for the film and well aligned in the perpendicular direction of the substrate surface. At this stage, we thought that we have single domain BMO films having an orthorhombic symmetry.

In order to study the in-plane epitaxy, we measured the reciprocal space mapping for two directions; x-ray diffr-action plane parallel to the STO [1-10] and [001] in-plane direction. First, we measured the reciprocal space maps around the STO (222) plane, as shown in Fig. 2(a). The existence of two x-ray wavelengths results in the separation of the STO substrate peaks into peaks corresponding to Cu $k_{\alpha 1}$ and $k_{\alpha 2}$ and demonstrates the accuracy of our mapping measurement. In this mapping experiment, one can easily find two important features. First, the horizontal position of the BMO film peak is the same as that of the STO (110) substrate peak, which demonstrates the coherent growth of a BMO film having in-plane lattice constants with the same values as those of the underlying STO substrate.
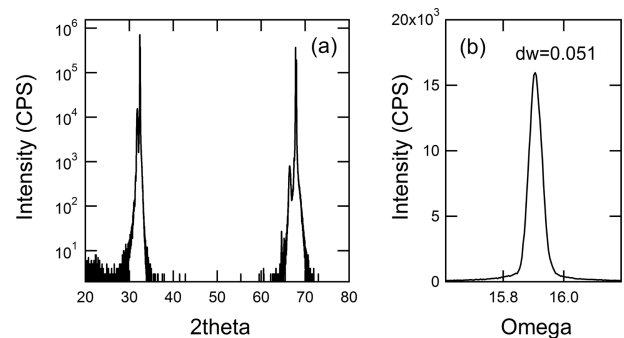
Fig. 1. BiMnO$_3$ thin film (t ~ 90 nm) grown on a nominally flat STO (110) substrate (a) XRD θ–2θ patterns. (b) The rocking curve for a BiMnO$_3$ film peak.

Second, we found that the BMO film showed three peaks. The central peak is the strongest among the three peaks and the out-of-plane lattice constants were estimated from this peak by assuming an orthorhombic symmetry in the film. The estimated value was consistent with that of the estimated from the θ–2θ pattern in Fig. 1(a). The
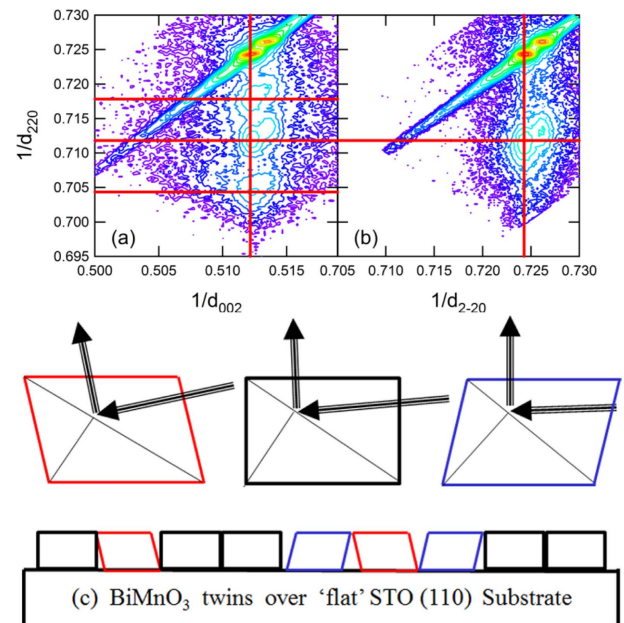
Fig. 2. (Color online) The existence of three domains in BiMnO$_3$ thin film (t ~ 90 nm) on a nominally flat STO (110) substrate (a) The mapping around the SrTiO$_3$ (222) plane shows one stronger film peak at the middle region together with two weaker peaks at upper and a lower region. (b) X-ray reciprocal space mapping around the SrTiO$_3$ (400) plane shows a very shaper for BiMnO$_3$ where the second BMO peak is from Cu kα2. (c) The existence of three twins of BiMnO$_3$ on top of a flat STO (110) substrate was suggested (One with orthorhombic symmetry, the other two with monoclinic symmetry).

other two peaks have a different vertical position. At first, this may imply that there are other novel BMO phases with orthorhombic symmetry and with a different value for the out-of-lattice constant with each other. But this is inconsistent with the sharp Rocking curve in Fig. 1(b).

Although we observed three peaks for the maps around the STO (222) plane, only one peak appeared in the reciprocal space maps around the STO (400) plane, as shown in Fig. 2(b). The vertical position of the film peaks in the Fig. 2(b) was the same as that of central BMO film peak in Fig. 2(a). So the unit cell of the domain corresponding to the central peak in Fig. 2(a) should have a rectangular orthorhombic. Moreover, the unit cell of the domain corresponding to the two sides BMO peaks in Fig. 2(a) should not come from the BMO phases with an orthorhombic symmetry and with a different value for the out-of-plane lattice constant.

The existence of multiple domains has been also reported for thin films of BiFeO₃, which is another multiferroic material. Jang *et al*. found four BFO domains for the film grown on STO (001) substrate. They used a miscut STO (001) substrate to reduce *four* BFO domains on non-miscut STO (001) substrate to *two* domains. From the two mapping data, we can conclude that we have three domains; one is of the orthorhombic symmetry and the other two are of the monoclinic symmetry. The single peak in Fig. 2(b) shows that the three domains have the same unit-cell volume. Figure 2(b) could explain the structure of the three domains of BMO on the nominally flat STO (110) substrate.

Since the existences of domains hamper the correct evaluation of physical properties, we tried to reduce the number of domains. Miscut substrates whose surface normal direction is not parallel to the principle axis of the substrate have been used to reduce twin problems in SrRuO₃, BiFeO₃, and CaHfO₃ [3, 12, 13]. Since the peak showing the existence of multiple domains of BMO appeared along the STO [001] direction, we used miscut STO (110) substrates with miscut angle along the STO [001] direction.

Figure 3(a) shows the θ−2θ patterns of a BMO film grown on top of an STO (110) substrate with a miscut angle of 1 degree. The BMO reflection peaks are clearly visible at the left of the STO (110) substrate peaks. The x-ray rocking curve of the BMO peak shown in the inset exhibited very narrow peak with FWHM as small as 0.047 degrees.

To study the effect of the miscut angle on the multiple domains, we again measured reciprocal space mapping. The mapping around the STO (400) plane shows only one peak and the vertical position of the peak located at the
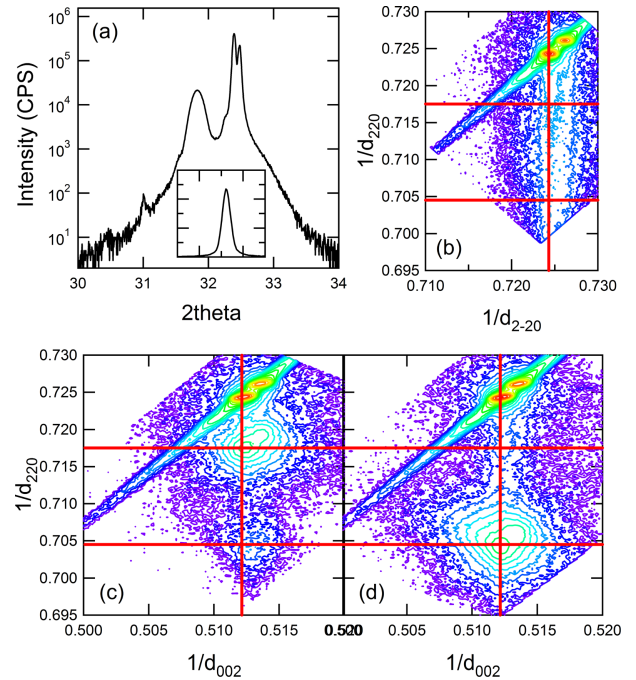
Fig. 3. (Color online) BiMnO₃ thin film (t ~ 90 nm) on an STO (110) substrate with a miscut angle of 1 degree. (a) XRD θ−2θ patterns and the rocking curve for a BiMnO₃ film peak. (b) X-ray reciprocal space mapping around the SrTiO₃ (400) plane shows a rather broad peak for BiMnO₃. (c) The mapping around the SrTiO₃ (222) plane shows one stronger film peak at upper region together with one much weaker film peak at the lower region. (d) The mapping around the SrTiO₃ (22-2) plane shows one weaker film peak at upper region together with one much stronger film peak at the lower region.

center of the vertical positions of the three BMO peaks in Fig. 2(a). It is quite notable that the peak is broader than the one shown in Fig. 2(b). Figure 3(c) shows the reciprocal space mapping around the STO (222) plane for the BMO film and the mapping around STO (22-2) plane in Fig. 3(d) was taken after rotating the sample by 180 degrees around the STO [110] direction. Each mapping shows one strong BMO peak but the vertical position is different, which clearly shows that BMO film has a *monoclinic* structure. Also, you can find another weak peak for BMO and no peak corresponding to the central BMO peak in Fig. 2(a) is visible. So we found the even one-degree miscut angle in the STO (110) substrate can favor strongly favor the one phase among the three phases shown in Fig. 2(a) though STO substrate itself has a cubic structure.

To study the efficiency of the miscut angle in stabilizing the single domain, we further tested the ability for a thicker film where the in-plane lattice constant deviates from that of the underlying substrate. Thus, we grew a
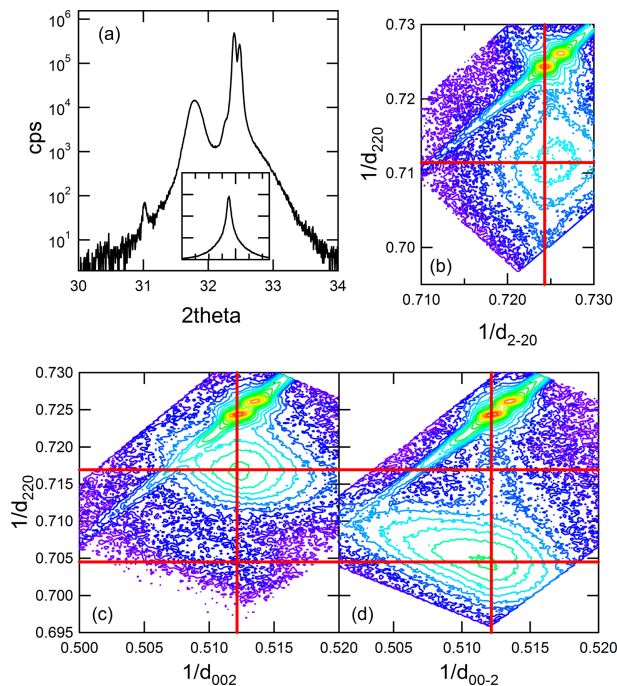
Fig. 4. (Color online) BiMnO$_3$ thick film (t = 200 nm) on an STO (110) substrate with a miscut of 1 degree. (a) XRD $\theta-2\theta$ patterns and inset showing the rocking curve for a BiMnO$_3$ film peak. (b) X-ray reciprocal space mapping around the SrTiO$_3$ (400) plane shows a strong peak for BiMnO$_3$. Note that the horizontal peak position of BMO film is different from that of the STO substrate. (c) The mapping around the SrTiO$_3$ (222) plane shows one stronger film peak at upper region together with one much weaker film peak at the lower region. (d) The mapping around the SrTiO$_3$ (22-2) plane shows one weaker film peak at upper region together with one much stronger film peak at the lower region.

200 nm thick BMO film on an STO (110) substrate with a miscut of 1 degree.

Figure 4(a) shows the $\theta-2\theta$ patterns of a thick (t ~ 200 nm) BMO film grown on top of an STO (110) substrate with a miscut angle of 1 degrees near the STO (110) peak region. The BMO reflection peak is clearly visible at the left of the STO (110) substrate peak. The x-ray rocking curve of the BMO peak is shown in the inset. The FWHM increased to 0.16 degrees which are 3 times larger than that of the thinner film shown in Fig. 1 and Fig. 3. The broadening of the rocking curve was estimated to come from the relaxed growth of the thicker film.

To confirm the relaxed growth behavior, we again measured reciprocal space mapping. The mapping around STO (400) plane as in Fig. 4(b) shows only one peak and the vertical position of the peak located at the center of the vertical positions of the three BMO peaks in Fig. 2(a). It is quite clear that the horizontal position of the BMO

peak shifted to the rightward with respect to that of the STO substrate. This relaxed growth behavior is consistent with the increased value of FWHM as shown in the inset of Fig. 4(a).

We found that increased thickness of the BMO film grown on top of an STO (110) substrate with a miscut of 1 degree resulted in the relaxed growth where the *grip* power of the interface is not strong enough to keep the same in-plane lattice constant of the film over the whole thickness. In this situation, we still want to check the *selection* power of the interface whether the miscut angle still can stabilize only one domain among the three domains in Fig. 2(a). Figure 4(c) and 4(d) show the reciprocal space maps around STO (222) plane and STO (22-2) plane, respectively. Quite clearly, each mapping shows one strong BMO peaks. Thus, we found the one-degree miscut angle in the STO (110) substrate can stabilize the one phase among the three phases even for thick BMO film.

It should be noted that we utilized both anisotropic (110) plane of cubic STO substrate and a miscut angle to generate more in-plane anisotropy, which removed 2-fold rotation symmetry of the STO [110] substrate around STO [110] direction. This demonstrates the importance of interface for the growth of metal oxide having low symmetry.

4. Conclusions

Pierre Curie stated that it is the symmetry breaking that creates physical properties. The existence of ferroelectricity in bulk BiMnO$_3$ should be investigated in a thin film with single domain due to the leakage problem. The film should be single domain without much grain boundary and should have a similar symmetry to that of bulk BiMnO$_3$; monoclinic symmetry. We studied the effect of miscut angle and film thickness on the symmetry of BiMnO$_3$ thin film. A flat SrTiO$_3$ (110) substrate resulted in a thin film with three domains of BiMnO$_3$ and 1 degree miscut in the SrTiO$_3$ (110) substrate resulted in dominant domain preference in BiMnO$_3$ thin film. This strong power of domain selection due to the step edge of the substrate was even efficient for the thick film which showed a relaxed growth behavior.

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