Observation of Resistance Switching in BiMnO\(_3\) Thin Film Grown on Nb-doped SrTiO\(_3\) (110) Substrate

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BiMnO\(_3\) has been assumed to be a very rare example of multiferroic materials. But the growth of BiMnO\(_3\) thin film with high quality itself was very challenging. So physical properties has been studied only marginally for this compound. Here we report the observation of resistance switching for twin free BiMnO\(_3\) thin film which was grown with high quality on the miscut Nb-doped SrTiO\(_3\) (110) substrate.

Keywords: BiMnO\(_3\), resistance switching, miscut substrate, multi-functional

1. Introduction

Metal oxides of ABO\(_3\) having a perovskite structure have multi-functionalities. These functionalities include ferromagneticity, ferroelectricity, resistance switching memory, colossal magnetoresistance, and high-temperature superconductivity [1-6]. In some cases, these functionalities coexist or even couple with each other in single compound [1]. Fabrication of thin film with high quality without twin has been an essential strategy to utilize and/or merge these wide functionalities into real devices. The epitaxial strain of single crystalline oxide substrate has contributed to stabilization of single crystalline ABO\(_3\) oxide films.

However ABO\(_3\) with lower symmetry often resulted in the twins in the thin films grown on atomically flat substrate [2]. Such a complex domain/twin structures can deteriorates the ferroelectric response of the system and also hinders the study of intrinsic transport properties [2]. A miscut SrTiO\(_3\) (001) substrate usually miscut angle alone either [100] or [010] direction means that [100] in-plane direction is not identical to [010] in-plane direction. This miscut SrTiO\(_3\) (001) substrate where the surface normal direction is not parallel to the principle axis of the substrate have been used to reduce twin problems in SrRuO\(_3\), BiFeO\(_3\), and CaHfO\(_3\) [2-4]. BiFeO\(_3\) is a very rare example of multi-ferroics where antiferromagnetism coexist with ferroelectricity with higher transition temperatures [1]. Thus this material has been studied most intensively among all multi-ferroic materials recent years. Moreover resistance switching behavior was also found for this material, which makes the material more interesting for application into novel devices [5, 6]. BiMnO\(_3\) has been expected to be a multi-ferroic material where ferroelectricity coexist with ferromagnetism. Bulk BiMnO\(_3\) has a monoclinic structure; \(a = 9.533\) Å, \(b = 5.606\) Å, \(c = 9.854\) Å and \(\beta = 110.667^\circ\) [7]. Asymmetric Bi was supposed to result in ferroelectricity and Mn was supposed to result in ferromagnetism.

Previously we reported the growth of BiMnO\(_3\) thin film on SrTiO\(_3\) (110) substrate with exceptional qualities [7, 8]. More importantly we found that BiMnO\(_3\) thin films can be grown without twins on the SrTiO\(_3\) (110) substrate with miscut. We adopted a miscut angle together with anisotropic (110) plane of cubic SrTiO\(_3\) substrate to generate more in-plane anisotropy, which removed 2-fold rotation symmetry of the SrTiO\(_3\) (110) substrate around SrTiO\(_3\) [110] direction. This demonstrated the importance of interface for the growth of metal oxide having low symmetry. We were the first group to use the miscut SrTiO\(_3\) (110) substrate. Then we found negative results on the existence of ferroelectricity in BiMnO\(_3\). In this report, we report the observation of resistance switching in BiMnO\(_3\) thin film.

2. Experimental

We grew thin films of BiMnO\(_3\) on a Nb-doped SrTiO\(_3\)
(110) substrates with miscut angles (2 degrees) using a pulsed laser deposition method [7, 8]. The details on the difficulty to get the stoichiometric BiMnO$_3$ thin film can be found in our previous report [7, 8]. In these reports, the clear ferromagnetic transition similar to that observed for bulk was confirmed [7, 8]. The thickness was estimated to be, $t \sim 80$ nm, using a field emission scanning electron microscope. To measure resistance switching properties, we used a probe station after depositing silver top electrode with aluminum adhesion layer on top of BiMnO$_3$. We used a high-resolution x-ray diffractometer to study the crystal structure of the BiMnO$_3$ films.

3. Results and Discussion

We first confirmed the phase purity of the grown BiMnO$_3$ thin film. Figure 1(a) shows the $\theta$–2$\theta$ patterns of a BiMnO$_3$ film grown on Nb-doped SrTiO$_3$ (110) substrate with a miscut angle of 2 degrees. For the SrTiO$_3$ substrate, we can see two well-separated peaks near $2\theta \sim 32.3$ degrees due to the existence of two wavelengths of x-ray corresponding to Cu $k_{\alpha 1}$ and $k_{\alpha 2}$. The clear separation of the substrate peaks demonstrates the accuracy of our mapping measurement. The BiMnO$_3$ peak is clear and strong at the left of the SrTiO$_3$ (110) substrate peaks. [The small peak near $2\theta \sim 31.0$ degrees is known to be the substrate peak due to spurious x-ray from the x-ray tube.] The full width at half maximum for x-ray rocking curve of the BiMnO$_3$ film peak was as small as $\sim 0.05$ degrees, as shown in the inset.

To confirm the twin-free growth of the BiMnO$_3$ film, we measured reciprocal space mapping for two directions; x-ray diffraction plane parallel to the SrTiO$_3$ [1-10] in-plane direction and x-ray diffraction plane parallel to the SrTiO$_3$ [001] in-plane direction. First, the horizontal positions of the BiMnO$_3$ film peaks in Fig. 1(b), 1(c), and 1(d) were the same as those of the SrTiO$_3$ (110) substrate peak, which demonstrates the coherent growth of the BiMnO$_3$ film. Thus in-plane lattice constants of the film are the same values as those of the underlying SrTiO$_3$ substrate. The mapping around SrTiO$_3$ (400) plane shown in Fig. 1(b) shows only one peak and the vertical position of the peak located roughly at the center of the vertical positions of each BiMnO$_3$ peaks in Fig. 1(c) and 1(d). It is quite notable that the peak in the (400) mapping is broader than the one in the (222) and the (22-2) mapping shown in Fig. 1(c) and 1(d). The out-of-plane lattice constants were estimated by simply assuming orthorhombic symmetry of the film and film peak in Fig. 1(b) and were consistent with that of the estimated from the $\theta$–2$\theta$ pattern in Fig. 1(a). The different vertical position of BiMnO$_3$ film peak in Fig. 1(c) and 1(d) demonstrates the monoclinic symmetry of the BiMnO$_3$ film as demonstrated previously [8].

Figure 2 show the resistance switching observed for our twin free BiMnO$_3$ thin film. In our previous report, we showed quite leaky Q-E curve for BiMnO$_3$ at room temperature and this leaky behavior existed even at $T = 150$ K [7, 8]. To avoid this leakage problem in the semi-conducting BiMnO$_3$, we used a pulse with a width of 250 ns (5 Volt and $\sim 2$ Volt) [9] while other group used AC measurement with frequency upto 1 MHz for BiMnO$_3$ (50-nm) thin films grown on conducting (001)-oriented 0.5 % Nb-doped SrTiO$_3$ [10]. It should be also stressed that we used a miscut Nb-doped SrTiO$_3$ (110) substrate to remove the twins of BiMnO$_3$ to minimize the leakage due to the existence of twin [8]. Another noticeable difference is that a miscut Nb-doped SrTiO$_3$ (110) substrate resulted in much lower crystal symmetry of BMO phase that flat Nb-doped SrTiO$_3$ (001) substrate [8]. The 5 V pulse resulted in the high resistance statues while $\sim 2$ V pulse resulted in the low resistance switching as shown in the Fig. 2. Both low resistance state and high resistance state

![Fig. 1. (Color online) BiMnO$_3$ thin film ($t \sim 90$ nm) on a SrTiO$_3$ (110) substrate with a miscut angle of 1 degrees. (a) XRD $\theta$–2$\theta$ patterns and the rocking curve for a BiMnO$_3$ film peak. (b) X-ray reciprocal space mapping around the SrTiO$_3$ (400) plane shows a rather broad peak for BiMnO$_3$. (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.](image-url)
showed a fluctuation of its resistance state with application of consecutive pulses. The on-off ratio defined by high resistance value denominated by low resistance value was less than about 3 which is quite smaller than ~100 reported for BiFeO\textsubscript{3} [5, 6]. Note that BiFeO\textsubscript{3} is insulating enough while BiMnO\textsubscript{3} is quite leaky. Usually the on-off ratio for metal oxides showing resistance switching behavior is higher for more insulating in the metal oxides. However the existence of resistance switching with clear two states is clearly verified for our BiMnO\textsubscript{3} thin film. Thus we demonstrate that BiMnO\textsubscript{3} is multi-functional by including both ferromagnetism and resistance switching. The mechanism of the resistance switching in BiMnO\textsubscript{3} is not yet clear and need to be done in the future.

4. Conclusions

The existence of ferroelectricity in bulk BiMnO\textsubscript{3} should be investigated in thin film 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\textsubscript{3}, monoclinic symmetry. We verified the existence of resistance switching in twin-free high quality BiMnO\textsubscript{3} thin film grown on Nb-doped SrTiO\textsubscript{3} (110) substrate.

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