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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 β = 110.667° [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 $SrTiO_3$

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(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 ~ 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 θ–2θ 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 $k_{\alpha1}$ and $k_{\alpha2}$. 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 ~ 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 θ–2θ pattern in Fig. 1(a). The different vertical position of

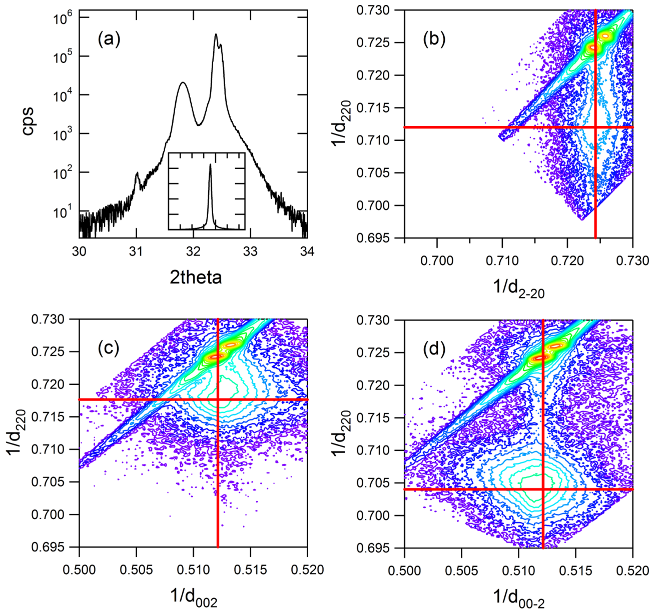

Fig. 1. (Color online) $BiMnO_3$ thin film ($t \sim$ 90 nm) on a $SrTiO_3$ (110) substrate with a miscut angle of 1 degrees. (a) XRD θ–2θ patterns and the rocking curve for a $BiMnO_3$ film peak. (b) X-ray reciprocal space mapping around the $SrTiO_3$ (400) plane shows a rather broad peak for $BiMnO_3$. (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.

$BiMnO_3$ 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 semiconducting $BiMnO_3$, we used a pulse with a width of 250 ns (5 Volt and −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 −2 V pulse resulted in the low resistance switching as shown in the Fig. 2. Both low resistance state and high resistance state

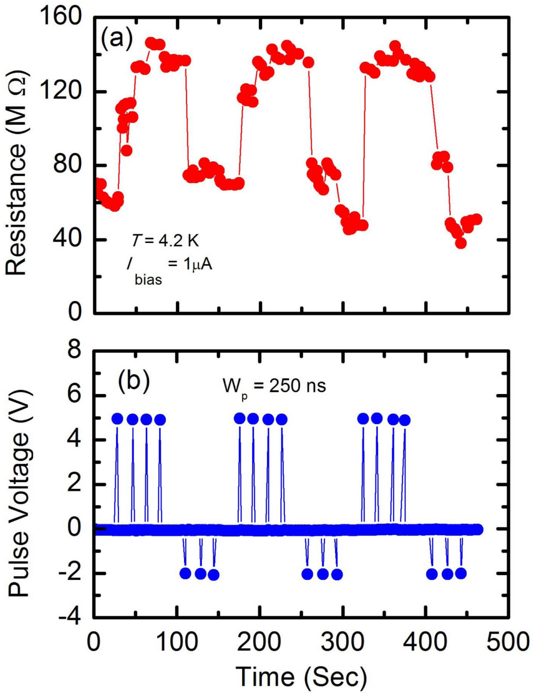

Fig. 2. (Color online) The change of resistance with application of voltage pulse was measured. Due to quite leaky nature of $BiMnO_3$, the measurement was done at T = 4.2 K and with very short pulse with width of 250 ns.

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 $BiFeO_3$ [5, 6]. Note that $BiFeO_3$ is insulating enough while $BiMnO_3$ 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 $BiMnO_3$ thin film. Thus we demonstrate that $BiMnO_3$ is multifunctional by including both ferromagnetism and resistance switching. The mechanism of the resistance switching in $BiMnO_3$ is not yet clear and need to be done in the future.

4. Conclusions

The existence of ferroelectricity in bulk $BiMnO_3$ 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 $BiMnO_3$; monoclinic symmetry. We verified the existence of resistance switching in twin-free high quality $BiMnO_3$ thin film grown on Nb-doped $SrTiO_3$ (110) substrate.

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References

[1] Y. Tokura, Science **312**, 1481 (2006). N. A. Spaldin and M. Fiebig, Science **309**, 391 (2005).
[2] H. W. Jang, D. Ortiz, S.-H. Baek, C. M. Folkman, R. R. Das, P. Shafer, Y. Chen, C. T. Nelson, X. Pan, R. Ramesh, and C.-B. Eom, Adv. Mat. **21**, 817 (2009).
[3] G. Koster, L. Klein, W. Siemons, G. Rijnders, J. S. Dodge, C. B. Eom, D. H. A. Blank, and M. R. Beasley, Rev. Mod. Phys. **84**, 253 (2012).
[4] B. W. Lee, C. U. Jung, M. Kawasaki, and Y. Tokura, J. Appl. Phys. **104**, 103909 (2008).
[5] A. Q. Jiang, C. Wang, K. J. Jin, X. B. Liu, J. F. Scott, C. S. Hwang. T. A. Tang, H. B. Lu, and G. Z. Yang, Adv. Mater. **23**, 1277 (2011).
[6] S. Hong, T. Choi, J. H. Jeon, Y. Kim, H. Lee, H. Joo, I. Hwang, J. Kim, S. Kang, S. V. Kalinin, and B. H. Park, Adv. Mater. **25**, 2339 (2013).
[7] B. W. Lee, P. Yoo, V. B. Nam, T. Kirstie, and C. U. Jung, Nanoscale Res. Lett. **10**. 10.1186/s11671-015-0759-9 (2015).
[8] U. Dash, N. V. Raveendra, and C. U. Jung, Journal of Alloys and Compounds **684**, 310e314 (2016).
[9] A. Odagawa, H. Sato, I. H. Inoue, H. Akoh, M. Kawasaki, Y. Tokura, T. T. Kanno, and H. Adachi, Phys. Rev. B **70**, 224403 (2004).
[10] R. Schmidt, J. Ventura, E. Langenberg, N. M. Nemes, C. Munuera, M. Varela, Mar Garcia-Hernandez, C. Leon, and J. Santamaria, Phys. Rev. B **86**, 035113 (2012).