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Crystal Structure and Electric/Magnetic Properties of Bi-related Perovskite Oxide thin Films Grown by Pulsed Laser Deposition Method

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Abstract: $BiFe_{1-x}Mn_xO_3$ thin films are grown by pulsed laser deposition (PLD) method on $SrTiO_3$(STO)(100) and (110) substrates. The observation of the the surface and the result of the reciprocal space mappings (RSMs) suggest the different crystal structure between the surface and the closer part to the interface. The surface of BFMO on STO(100) exhibits a sawtooth-like structure with the angle of 60 and 120 degrees between grains, suggesting the hexagonal surface structure. The results of RSMs on the other hand, indicate the orthorombic structure having a tilt of 0.2 degrees from the substrate crystal plane. The results of the surface morphology, RSMs, and the current-voltage curve suggest that the leakage current of BFMO films is caused by Poole-Frenkel model conduction.

1. Introduction

The aim of our study is to synthesize the novel multi-functional materials which show ferromagnetic (FM) and ferroelectric (FE) properties with a giant magnetoelectric effect at room temperature. It is well known that the two-dimensional (2D) electron gas at the $LaAlO_3$(LAO)/$SrTiO_3$(STO)(100) interface results in superconductivity and ferromagnetic ordering, even though the both materials are nonmagnetic insulator. In the [$CaFeO_3$/$BiFe_{1-x}Mn_xO_3$(BFMO)] superlattices, we expect the charge transfer through the interface, like LAO/STO interface, with an electric field applied to realize and control the $3d^5$-$3d^4$ state, which shows ferromagnetic superexchange interaction around the interface according to the Kanamori-Goodenough rules. The atoms of Bi and, Fe and Mn in the superlattices are to induce the FE property and FM interaction between $3d^5$ and $3d^4$, respectively. In order to realize the superlattices with quite flat interface at an atomic level, growth condition have to be precisely controlled. In this study, we report the fabrication process, crystal structures, and electric/magnetic properties of the BFMO films. All films were deposited by pulsed laser deposition (PLD) method.

2. Experimental

For films growth, STO(100) and STO(110) substrate were used. The STO(100) and STO(110) substrates was ultrasonically cleaned in acetone and ethanol. The cleaned substrates was soaked in pure water for 30min. The substrates surface was etched by a Buffered HF (BHF) (Daikin Industries, Ltd, pH=5.0) for 45 sec, immediately rinsed by pure water. The etched STO(100) substrate was annealed at 920 ºC for 6 h in air. The etched STO(110) substrate was annealed at 1100 ºC for 2 h in air. All films were grown by the PLD method using excimer laser of KrF 248 nm. Typical ablation conditions were as follows; the substrate temperature, energy density, repetition rate, oxygen partical pressure, and the distance between substrate and target were 670~700 ºC, 2.4~2.7 J/cm^2, 2~4 Hz, 20 Pa, 55 mm, respectively. All films were post-annealed at 0.1 MPa oxygen atmosphere with the rate of 10 ºC/min down to room temperature. The targets were prepared by traditional solid solution method and Pechini method.

3. Results and Discussion

3.1 BFMO on STO(100)

Fig. 1 shows the surface morphology of the (a) annealed STO(100) substrate and (b) BFMO thin film grown on STO(100). The step-terraces structure was observed on the surface treated STO(100). On the other hand, the surface of BFMO film exhibited a sawtooth-like structure with the angle of 60 and 120 degrees between grains, suggesting the hexagonal structure of the BFMO film.

Fig. 2 shows the reciprocal space mappings (RSMs) around (a) STO(003), (b) STO(103), and (c) STO(113). Nothing changed in the position and the intensity of the peaks in all RSMs when rotating the substrate along the ϕ direction. From the result of (a), two

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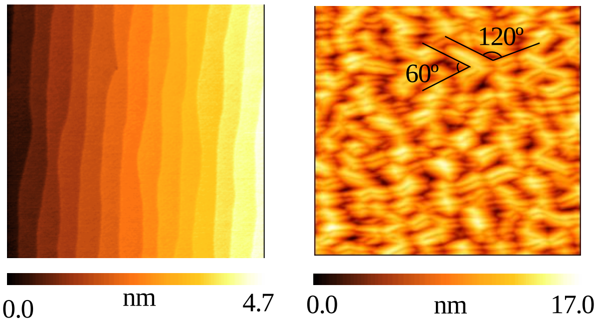
split peaks were observed, indicating that the BFMO film grew with the tilting angle of 0.20° from the substrate crystal plane. Two split peaks appeared in (b) and (c) as well. The crystal structure is expected to be orthorhombic from the results of RSMs.

The observation of the surface and the result of the RSMs suggest the different crystal structure between the surface and the closer part to the interface. This difference can be explained by the degree of the stress from the substrate. We expect that the structure of BFMO thin film was orthorhombic at an initial stage of the crystal growth due to the stress from substrate. On the other hand, with increasing the film thickness, the grains become a hexagonal due to the relaxing.

The electric property was also investigated. In ferroelectric perovskite oxides, leakage mechanisms are commonly classified into three mechanisms; (i) space-charge-limited conduction (SCLC), (ii) Schottky emission, and (iii) Poole-Frenkel emission. The mechanisms can be estimated from current-voltage curves.



(a) STO(100) substrate (2μm×2μm)　(b) BFMO thin films (2μm×2μm)

Fig. 1 The surface morphology

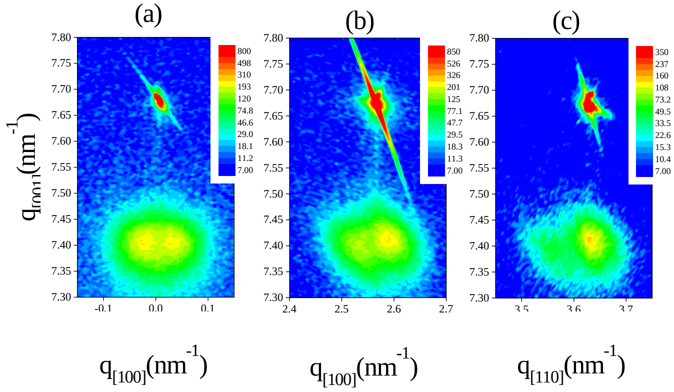


Fig. 2 The RSMs around (a)STO(003), (b)STO(103), (c)STO(103)

Fig. 3 shows the leakage current characteristics of BFMO on STO(100). If SCLC were the dominant leakage mechanism, a straight having a slope 2 fit to the data in log J vs log E. The slope of our film, 4.3 and 3.3 indicate the presence of other leakage mechanisms. The Schottky and Poole-Frenkel emission can be investigated by a straight fit to the data in log J vs $E^{1/2}$ and log σ vs $E^{1/2}$, respectively. Both models can explain our data as shown in Fig. 3 (ii) and (iii). Schottky emission is interface-limited conduction. This conduction mechanism arises from a difference in Fermi levels between a metal (electrode) and an insulator or semiconductor (films). Therefore, we expect that our BFMO film is Poole-Frenkel conduction because the film has a lot of grain boundaries from the results of the surface and RSMs.

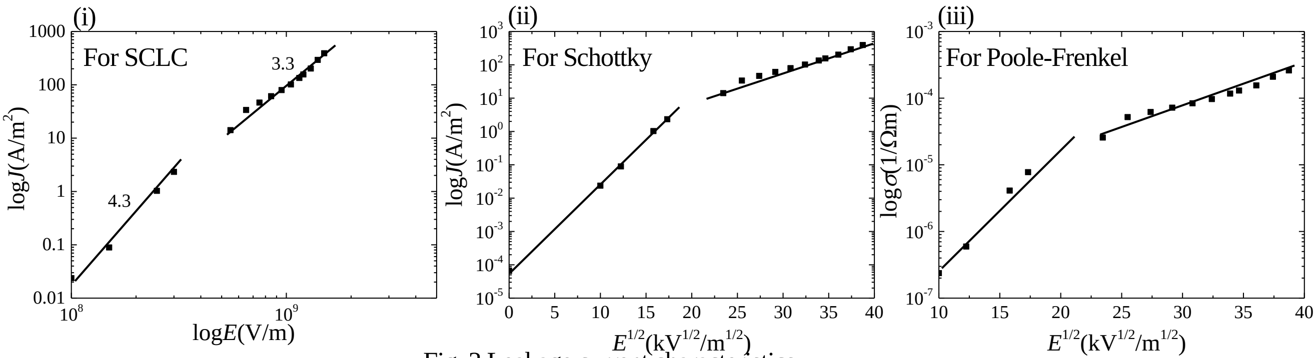


Fig. 3 Leakage current characteristics
(i) log J vs log E　(ii) log J vs $E^{1/2}$　(iii) log σ vs $E^{1/2}$

4. **Summary**

The BFMO thin film were grown on STO(100) and STO(110) substrates using the PLD method. From the surface and RSMs, the structure of BFMO grown on STO(100) was orthorhombic at an initial stage of the crystal growth due to the stress from substrate. On the other hand, with increasing the film thickness, the grains become a hexagonal due to the relaxing. From the leakage current characteristics, we expect that our BFMO film is Poole-Frenkel conduction because The film has a lot of grain boundaries from the results of the surface and RSMs.