Electric and Magnetic Properties of BiFe$_{1-x}$Mn$_x$O$_3$ Thin Films and CaFeO$_x$/BiFe$_{1-x}$Mn$_x$O$_3$ Superlattices

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The BiFe$_{1-x}$Mn$_x$O$_3$(BFMO) film shows monoclinic structure distorted along the <110> direction, while high quality [CaFeO$_x$(CFO)/BFMO] superlattice grows with tetragonal structure, lattice parameter of which in-plane is fit to that of Nb doped SrTiO$_3$(001) substrate. The BFMO film and the [CFO/BFMO] superlattice show similar M-H curves and saturation magnetic moment as a function of temperature. Magnetic moment rapidly increases in low magnetic field region and then gradually develops and saturated in high field region at 10 K. At 300 K, magnetic moment saturates in low magnetic field. As a temperature increases, saturation magnetic moment per magnetic ion rapidly increases above 10K, and then gradually reduces. The magnetic moment at 300K of BFMO is 0.107µ$_B$ higher than 0.034µ$_B$ detected in the [CFO/BFMO] superlattice, probably due to the thin BFMO layer in the superlattice. Estimated $T_c$ of the BFMO film and the superlattice is 600 K and 500K, much higher than room temperature. Leakage current behavior indicates the Fowler-Nordheim tunneling and Schottky emission at Au/BFMO interface and Poole-Frenkel hopping conduction in the BFMO layer.

Key words: BiFe$_{1-x}$Mn$_x$O$_3$, CaFeO$_x$, Superlattice, PLD, multiferroic, magnetoelectric

1. INTRODUCTION
The aim of our research is to synthesize the novel multi-functional materials which show ferromagnetic (FM) and ferroelectric (FE) properties with a giant magnetoelectric effect at room temperature[1-8]. It is well known that the two-dimensional (2D) electron gas at the LaAlO$_3$(LAO)/SrTiO$_3$(STO)(001) interface results in superconductivity and ferromagnetic ordering, even though the both materials are nonmagnetic insulator[9-17]. In the case of [CaFeO$_x$(CFO)/BiFe$_{1-x}$Mn$_x$O$_3$(BFMO)] ($x=0.1$ or 0.2) superlattices, we expect the charge transfer through the interface, like LAO/STO interface, controlled by an application of external electric field normal to the superlattices surface. The charge transfer could realize a $3d^0$-$3d^8$ state, which induce ferromagnetic superexchange interaction around the interface according to the Kanamori-Goodenough rules[17-19]. In order to obtain an atomic level flat interface in the superlattices, growth condition have to be precisely controlled. In this paper, we report the fabrication process, crystal structures, and electric/magnetic properties of the BFMO film and [CFO/BFMO] superlattice.

2. EXPERIMENTAL
For films growth, Nb doped STO(NSTO)(001) substrates were used. The substrates were rinsed ultrasonically in acetone and ethanol. Surface treatment was carried out as follows. The cleaned substrates were maintained in deionized water for 30 min and soaked in buffered HF (BHF) (Daikin Industries, Ltd., BHF 120, pH = 5.0) for 45 sec using ultrasonic bath. After chemical treatment, the substrates were annealed at 920 °C for 6 hours in air.

All films were deposited by pulsed laser eposition (PLD) method using KrF excimer laser with high-pressure reflection high energy electron diffraction (RHEED) equipment. Typical ablation condition of heater temperature, energy density, spot size at a target, repetition rate and oxygen partial pressure were 670 °C, 2.6 J/cm$^2$, 1.8 mm$^2$, 4 Hz, 20 Pa, respectively. Films were post-annealed at 0.1 MPa oxygen atmosphere with the rate of 10 °C/min down to room temperature. In order to deposit accurate thickness in each layer of [CFO/BFMO] superlattice, the growth rate of the LaFeO$_3$ (LFO) film was referred. The deposition rate ratio of CFO and BFMO to LFO was determined by synthesizing CFO/LFO and BFMO/LFO bilayer in advance. As the [CFO/BFMO] superlattice was deposited, seven LFO layers were initially grown monitoring the RHEED oscillation, then required number of pulses to deposit seven CFO and BFMO layers was alternately irradiated to targets, and the deposition were repeated for 14 times[20,21].

All films were evaluated by RHEED, x-ray diffraction (XRD), x-ray reflection (XRR), reciprocal space mapping (RSM) using one dimensional detector (VĂNTEC-1)
(Bruker D8 Discover), electrical characterization (YOKOGAWA 7651 and KEITHLEY 6430) and magnetic properties (Quantum Design Inc., MPMS3). For electrical characterization, Au electrode with the size of 200 µm² were sputtered through a metal mask. The surface morphology was investigated by a scanning probe microscopy (SII Nanotechnology NanoNavi Station).

3. RESULT & DISCUSSION
3.1 BFMO film
Figure 1 shows the surface morphology of BFMO thin film and line profile. There were many trenches with the depth of several nanometers. However focusing on the surface structure on one grain, unit step was observed as shown in line profile.

The RSMs of BFMO thin film were detected around (a) STO(103), (b) STO(113) and (c) STO(-1-13) as shown in Fig. 2. Two peaks in (a) and three peaks in (b) and (c) were observed. Dashed lines noted the observed peaks position. In the RSMs of (b) STO(113), and (c) STO(-1-13), the intensity of the peaks I and II were switched[22]. From the appearance of the two peaks and the three peaks around STO(103) and STO(113), respectively, and switching of the I and II peaks, the structure of the grown BFMO thin film was monoclinic with four grains distorted along the <110> direction of STO substrate.

Figure 3 shows the magnetization curves ($M$-$H$) of the BFMO thin film measured at (a) 10 K and (b) 300 K with a magnetic field applied normal to the plane. Vertical axis is magnetic moment ($\mu_B$) per magnetic ion. The diamagnetic, paramagnetic, and antiferromagnetic contribution was excluded by subtracting a linear function. The linear function was given by fitting  in higher magnetic field region. There were low field saturation region and high field saturation region around 0.5 T, see inset graph, and 4 T, respectively, at 10 K. However at (b) 300 K, there was only low field saturation region. The $M$-$H$ curves indicate the presence of two kinds of ferromagnetic interaction at low temperatures. The value of saturation magnetic moment at 300 K was 0.107$\mu_B$, which is 10 times larger than that of bulk BFMO[23].

Figure 4 shows the saturation magnetic moment per magnetic ion versus temperature of the BFMO film. Saturation magnetic moment rapidly decreased higher than 10 K, then was gradually reduced. As shown in Fig 3(a), gradual increase of magnetic moment in high magnetic field region is expected to be caused by the developed
magnetic moment detected at 10 K. Inset graph shows normalized saturation magnetic moment, $M/M_s$, as a function of normalized temperature, $T/T_c$, using the results of $M$-$H$ curves detected higher than 50 K. The plots are experimental results and the solid line is drawn using the Brillouin function with total angular momentum $J=5/2$ assuming the saturation magnetic moment at 0 K and Curie temperature $T_c$. The estimated $T_c$ of the BFMO film was approximately 600 K much higher than room temperature. The ferromagnetic interaction is expected to be attributed to Mn$^{3+}$-$O$-$Fe^{3+}$ superexchange interaction and/or film strain.

Figures 5 (a-d) show the leakage current characteristics of Au/BFMO/NSTO/Au film. In all leakage current measurements Au electrode deposited on NSTO substrate was grounded. Positive voltage was applied to the Au electrode deposited on BFMO film. We discussed five mechanisms to explain the leakage current such as (a) ohmic and space-charge-limited conduction (SCLC), (b) Fowler-Nordheim (FN) tunneling, (c) Schottky emission, (d) Poole-Frenkel (PF) emission[24-28]. As ohmic or SCLC are the dominant leakage mechanism, a straight line with a slope of one or two are able to be fit to the data in log $J$ vs. log $E$ graph. From the result of figure 5 (a), between 10 K and 150 K, the value of the slope was higher than three that indicate the presence of other leakage mechanisms. At 200 K and 300 K in low electric field, the plot are linear with a slope with approximately one and two indicating ohmic and SCLC mechanism.

As the leakage current is dominated by the FN mechanism, a linear relation between $\ln (J/E^2)$ and $(1/E)$ with negative slope should be observed. Figure 5 (b) shows $\ln (J/E^2)$ vs. $(1/E)$ detected from 10 K to 300 K. The leakage current show FN tunneling behavior at 10, 50, 100 and 150 K in whole electric field region. However at 200 and 300 K, the FN tunneling behavior was observed at higher electric field.
As shown in Fig.5(c) and (d), the Schottky and PF emission can be investigated by a straight fit to the data in ln J vs. $E^{1/2}$ and ln $\sigma$ vs. $E^{1/2}$, respectively. From the results of figure 5 (c) and (d), leakage currents show Schottky and PF emission at 200 and 300 K in high electric fields. Lower than 150 K, the shape was seemed like inverse of “S” character.

From the results of those leakage current consideration, it is found to be quite complicated to explain leakage current mechanism consistently. However, what we are not able to understand is appearance of ohmic conduction at low electric field, thought the FN tunneling and Schottky emission might be due to Au/BFMO interface. The hopping conduction is expected to originate from shallow potential well of the BFMO film because of a deficiency of Bi and/or oxygen.

3.2 [CFO/BFMO] superlattice

[CFO/BFMO] superlattice showed a smooth surface with a step-terrace structure. Satellite peaks and Laue oscillations were clearly observed in a XRD 26-0 spectrum and RSMs around NSTO(003), (103), and (113). As a result, the calculated number of unit of deposited CFO and BFMO was 6.34 and 7.78 units. The in-plane lattice constant of [CFO/BFMO] superlattice was fitted to that of the NSTO(001) substrate. The full width at half maximum (FWHM) of the rocking curve was 0.0572 degrees. High quality tetragonal [CFO/BFMO] superlattice was obtained.

Figure 6 shows the magnetization curves of the [CFO/BFMO] superlattice measured at (a) 10 K and (b) 300 K with a magnetic field applied normal to the film plane. Magnetic moment rapidly increased at low field up to 0.1 T and then gradually developed and saturated at high field around 5 T at 10 K. At 300 K, magnetic moment saturated in low magnetic field. These M-H behaviors were similar to the results of BFMO film as shown in Figs.3(a) and 3(b). The value of saturation magnetization at 300 K was 0.034 $\mu_B$, which is 2 times larger than that of bulk BFMO[23].

Figure 7 shows the saturation magnetic moment per magnetic ion – temperature curves of the [CFO/BFMO] superlattice. In the case of the superlattice, the magnetic ion in the M-H curves is Fe or Mn ions in BFMO layer, not in the CFO layer, because the CFO is antiferromagnetic material with Néel temperature, $T_N$, of 115 K. Similar to the result of BFMO film as shown in Fig.4, the magnetic moment was intensively reduced higher than 10 K. Inset graph shows the $M/N$ as a function of $T/T_C$ using measured saturation magnetic moment higher than 50 K. The plots were experimental results and the solid line was drawn using the Brillouin function assuming the $M_S$ at 0 K and $T_C$. The estimated Curie temperature of the [CFO/BFMO] superlattice was 500 K much higher than room temperature.

In this paper magnetic and electric properties normal to the BFMO film surface were investigated. Band bending at the interface of Au and BFMO film induce the FN tunneling and/or Schottky emission. Hopping conduction in the BFMO film was reasonable as considering the Bi and/or oxygen deficiency. However comparing the saturation magnetic moment and estimated $T_C$ between BFMO film and [CFO/BFMO] superlattice, obtained results were sufficiently unique. The magnetic moment per magnetic ion at 300K of BFMO was 0.107 $\mu_B$, higher than 0.034 $\mu_B$ detected in the [CFO/BFMO] superlattice. In addition, the estimated $T_C$ of the BFMO film 600 K was also higher than 500 K estimated in the superlattice. The number of unit of each layer in superlattice is approximately seven. The reduced value of saturation magnetic moment and $T_C$ in superlattice is expected to derive from thin thickness, which is less than three nm in BFMO layer. The three dimensional ferromagnetic interaction is not enough in the seven BFMO layer. From another perspective, decreasing the number of layer of BFMO in the superlattice, both of saturation magnetic moment and $T_C$ might be reduced to zero and less than room temperature are predicted. In that superlattice, induced ferromagnetic property is expected by an electron transfer through the interface with an application of an electric field, because ferromagnetic interaction is developed between neighbor BFMO layers and around an interface in superlattice. From the consideration mentioned above, ferromagnetic interaction is expected to be induced by an electric field applied at room temperature.

![Fig.6 M-H curves of the [CFO/BFMO] superlattice measured at (a) 10 K and (b) 300 K with a magnetic field applied perpendicular to the film surface. Because the detected magnetic moment included diamagnetic of the substrate, ferromagnetic, antiferromagnetic, and paramagnetic of superlattice, it was difficult to extract only ferromagnetic component at 300 K, especially high magnetic field.](image-url)
Degrees. High quality tetragonal [CFO/BFMO] lattice constant of [CFO/BFMO] superlattice was fitted to.

As a result, the calculated number of unit of deposited T

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considering the Bi and/or oxygen deficiency. However higher than 10 K. Inset graph shows the

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100 K, leakage currents show

results of figure 5 (c) and (d), leakage currents show

high field around 5 T at 10 K. At 300 K, magnetic

magnetic moment as a function of temperature.

Magnetic moment rapidly increased at low field

plane. Magnetic moment rapidly increased at low field

[CFO/BFMO] superlattice measured at (a) 10 K and (b)

oscillations were clearly observed in a XRD 2

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like inverse of “ character.

Figure 7 shows the saturation magnetic moment per

N, of B, which is 2 times

M

B detected in the [CFO/BFMO] superlattice is approximately seven. The reduced value

superlattice. In addition, the estimated

is expected to be induced by an electric field applied at

interaction is developed between neighbor BFMO layers

an application of an electric field, because ferromagnetic

hardness, coercivity, and magnetic moment were

several times greater in the BFMO film than in the

interfacial reaction layer. Magnetization of the

BFMO film and the [CFO/BFMO] superlattice showed similar M-H curves and saturation magnetic moment as a function of temperature. Magnetic moment rapidly increased in low magnetic field at 10 K. At 300 K, magnetic moment saturated in low magnetic field. As a temperature increased, saturation magnetic moment per magnetic ion rapidly decreased above 10K, and then gradually reduced. The magnetic moment at 300K of BFMO was 0.107μB higher than 0.034μB detected in the [CFO/BFMO] superlattice. In addition, the estimated Tc of the BFMO film 600K was also higher than 500K estimated in the superlattice.

From the results of electric measurements normal to the surface of the BFMO film, the FN tunneling and Schottky emission is might be due to Au/BFMO interface, and PF hopping conduction is expected to originate from shallow potential well of the BFMO film.

We expect the control of the ferromagnetic interaction strength in the [CFO/BFMO] superlattice by varying the number of units of CFO and BFMO layer. Actually the Tc of the superlattice with seven units BFMO layer is lower than that of the BFMO film. Reducing the thickness of the BFMO layer to be paramagnetic at room temperature, ferromagnetic interaction is induced by an electron transfer with electric field applied.

5. REFERENCES

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