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Structural, magnetic, and ferroelectric properties of multiferroic $BiFeO_3$ film fabricated by chemical solution deposition

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Polycrystalline $BiFeO_3$ film has been fabricated by a chemical solution deposition on $Pt/Ti/SiO_2/Si(100)$ substrates. A ferroelectric hysteresis loop showed a high remanent polarization of 47 $\mu C/cm^2$ at room temperature. Leakage current density was on the order of 10^{-1} A/cm^2 at 100 kV/cm, indicating the high leakage current density in the present $BiFeO_3$ film. The leakage current mechanism could be considered as follows: Ohmic conduction at low electric field and Poole-Frenkel trap-assisted conduction appeared as the electric field increased, and space-charge-limited current started at a high electric field. Weak ferromagnetism was observed at room temperature, and magnetic coercivity increased to 0.5 kOe with small remanent magnetization of 2 emu/cm^3 at 10 K. In order to investigate the magnetoelectric effect of the $BiFeO_3$ film, the ferroelectric hysteresis loop was measured under the magnetic field of 5 kG at room temperature.
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I. INTRODUCTION

Multiferroic materials that have coupled magnetic, electric, and structural order parameters leading to a magnetoelectric (ME) effect have attracted much interest as a candidate material for a future multivalued memory system. $BiFeO_3$, one such multiferroic material, has a rhombohedrally distorted perovskite structure [space group: $R3c$ (Ref. 1)] with a relatively high ferroelectric Curie temperature [T_C=1123 K (Ref. 2)] and a high Néel temperature [T_N =653 K (Ref. 3)]. The $BiFeO_3$ has an advantage over the other multiferroic materials such as $BiCoO_3$,[4] $BiCrO_3$,[5] etc., from the viewpoint of film application, because these bulk ceramics require synthesis under high pressure, and it is necessary to promote epitaxial growth by using a single crystal substrate in order to fabricate the film specimen.[6] Therefore, recently, many results concerning both the bulk and the film structure in the $BiFeO_3$ materials have been reported and revealed that the film structure enhances the ferroelectric properties with the high leakage current in this material.[7,8] A few reports have discussed the mechanism of the leakage current of the $BiFeO_3$ film, but the exact mechanism has not yet been determined. By contrast, the magnetic properties of the $BiFeO_3$ film have not been intensively studied.

In this paper, we systematically investigate the magnetic and ferroelectric properties of $BiFeO_3$ films fabricated by a chemical solution deposition (CSD) substrates and discuss the leakage current mechanism as well as low temperature magnetic properties.

II. EXPERIMENTAL PROCEDURE

$BiFeO_3$ film was fabricated by CSD on $Pt/Ti/SiO_2/Si(100)$ substrates. Postdeposition annealing was performed by a rapid thermal annealing at 823 K for 10 min in air. The film thickness was 236 nm. The film structure was determined by a conventional $\theta/2\theta$ x-ray diffraction (XRD, Cu $K\alpha$) pattern as well as an atomic force microscopy (AFM) image. Ferroelectric hysteresis loops were performed by making use of a high frequency 100 kHz system produced by TOYO Corporation (FCE-1A-type ferroelectric test system). Leakage current density was measured by HP 4140B. A driving voltage was applied to the bottom electrode. The magnetic properties were measured by a superconducting quantum interference device (SQUID) magnetometer.

III. RESULTS AND DISCUSSION

A. Film structure

Figure 1 shows the x-ray diffraction pattern for the film specimen followed by postdeposition annealing at 823 K for 10 min in air. The polycrystalline $BiFeO_3$ film was formed after the annealing and no second phase could be observed in the x-ray diffraction pattern.

Figures 2(a) and 2(b) show the AFM images of the $BiFeO_3$ film, and Fig. 2(c) shows the line profile of the AFM

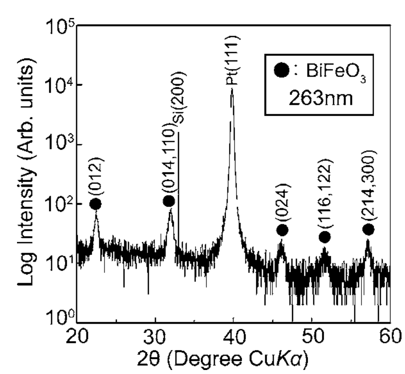

FIG. 1. An X-ray diffraction pattern for a $BiFeO_3$ film. A polycrystalline $BiFeO_3$ film was formed after annealing at 823 K for 10 min.

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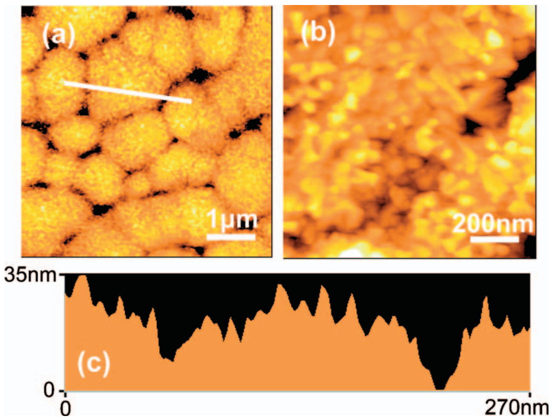

FIG. 2. AFM images for $BiFeO_3$ film [(a) and (b)] and a line profile of the AFM image (c).

image. The interstice space could be seen among the grains as shown in Fig. 2(a). The grain size estimated from the AFM image in Fig. 2(a) was about 2 μm. In order to understand the surface morphology of each grain at the submicron scale, we measured the line profile from the AFM image in Fig. 2(a). The small projections were formed on each grain and the average projection interval was about 60–80 nm. As shown in Fig. 2(b), the AFM image in the small area revealed that grains of size of several tens of nanometers were formed, which indicates that 2-μm-sized grains were composed of small grains of several tens of nanometers in diameter.

B. Ferroelectric properties

Figure 3 shows the ferroelectric hysteresis loops of the $BiFeO_3$ film measured without an applied magnetic field (a), as well as under an applied magnetic field of 5 kG (b). These measurements were performed using the high frequency of a 100 kHz measurement system. The remanent polarization of the $BiFeO_3$ film was 47 $\mu C/cm^2$ and the electric coercive field was 139 kV/cm at room temperature without a magnetic field. The remanent polarization was larger than that of the polycrystalline lead zirconate titanate (PZT) films.[9] As mentioned above, $BiFeO_3$ material has advantages over PZT because the material possesses not only ferroelectricity but also antiterromagnetism with a small spin canting system due to the parasitic magnetism, and therefore this material can expect a ME effect. For this reason, we measured the ferroelectric hysteresis loop under the magnetic field. The result is shown in Fig. 3(b). However, we could not observe

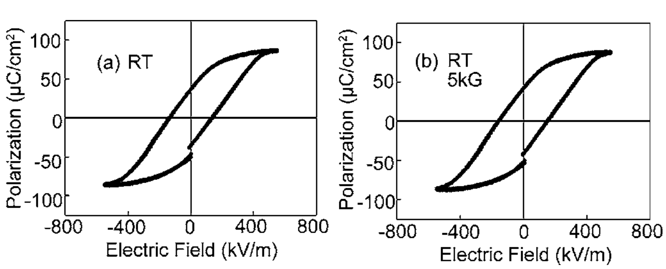

FIG. 3. *P-E* hysteresis loops for $BiFeO_3$ films without a magnetic field (a) and under the magnetic field of 5 kG (b). No difference can be seen in both *P-E* hysteresis loops.

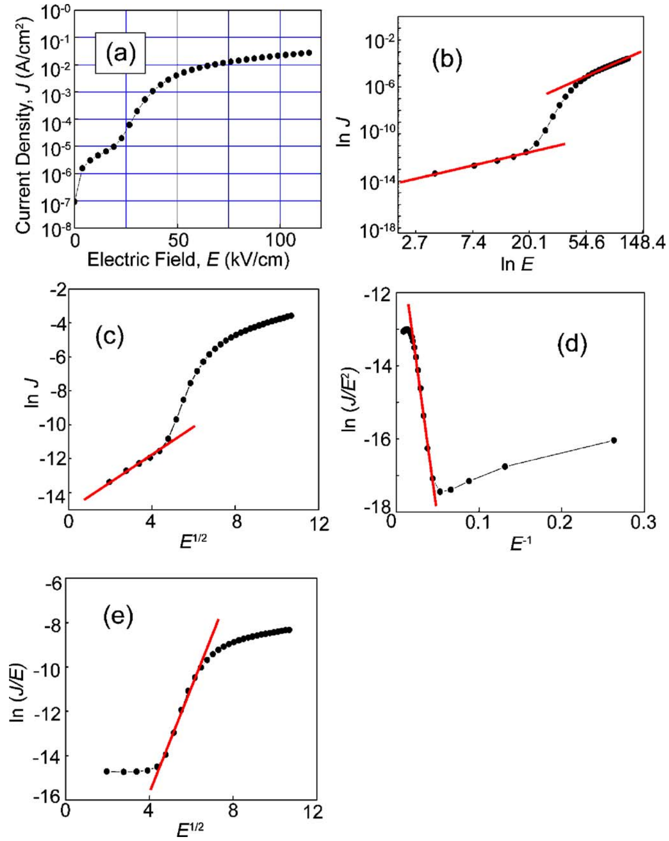

FIG. 4. Leakage current density (J) vs electric field (E) (a), double logarithm (b), $\log J$ vs $E^{1/2}$ (c), $\log(J/E^2)$ vs $1/E$ (d), and $\log(J/E)$ vs $E^{1/2}$ (e) plots for the $BiFeO_3$ film measured at room temperature.

obvious differences in the ferroelectric hysteresis loop when applying the magnetic field of 5 kG at room temperature.

Figure 4 shows the (a) leakage current density (J) versus electric field (E), (b) double logarithm, (c) $\log J$ vs $E^{1/2}$, (d) $\log(J/E^2)$ vs $1/E$, and (e) $\log(J/E)$ vs $E^{1/2}$ plots for the $BiFeO_3$ film measured at room temperature. As shown in Fig. 4(a), the leakage current density was on the order of 10^{-1} kV/cm at 100 kV/cm, indicating a high leakage current density in the present $BiFeO_3$ film. This result is consistent with other reports. However, only a few reports have discussed the mechanism underlying the leakage current. Hence, the theme of the leakage current density is still on the table even if it is an important issue from the viewpoint of memory application. Next, we will discuss the leakage current mechanism of the $BiFeO_3$ film. In Fig. 4(a), three kinds of the leakage current behavior could be observed. First, we will discuss the mechanism of the interfacial limited leakage current taking into consideration Schottky emission. By making use of Schottky emission, the relative permittivity and barrier height were estimated to be 0.4 and 0.6 eV, respectively [Fig. 4(c)]. On the other hand, the inclination at a low electric field in the double logarithm plots as shown in Fig. 4(b) was around 1.1–1.2, indicating occurrence of Ohmic conduction at the low electric field. It is difficult to determine the conduction mechanism at low electric field. Ohmic conduction seems to be adaptable compared to the Schottky-emission conduction at low electric field. The inclination at a high electric field in the double logarithm plots in

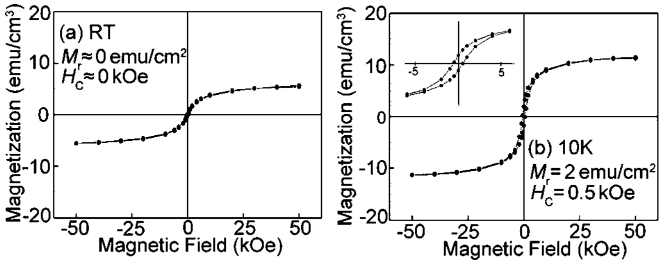

FIG. 5. *M-H* hysteresis loops for the $BiFeO_3$ film at 300 and 10 K, respectively.

Fig. 4(b) was around 2, indicating that the leakage current behavior at high electric field was dominated by space-charge-limited current (SCLC). Next, we discuss the leakage current mechanism before the start of the SCLC. The barrier height deduced from the Fowler-Nordheim equation was around 0.019 eV [Fig. 4(d)]. This barrier height is quite small for the case of Fowler-Nordheim tunneling conduction. The relative permittivity calculated by using the Poole-Frenkel equation was around 0.1–0.2 [Fig. 4(e)]. Here, we considered the leakage current mechanism to be as follows: Ohmic conduction at low electric field and Poole-Frenkel trap limited conduction appeared as the electric field increased and SCLC starts at a high electric field.

C. Magnetic properties

Figures 5(a) and 5(b) show the magnetic hysteresis loops for the in-plane direction measured at 300 and 10 K, respectively. The magnetic hysteresis loop at room temperature is a typical shape in parasitic ferromagnetic $BiFeO_3$ films. The saturation magnetization of the $BiFeO_3$ film was 5 emu/cm^3, and the remanent magnetization as well as the magnetic coercivity could not be observed at room temperature. As the temperature dropped to 10 K, the saturation magnetization, the remanent magnetization, and the magnetic coercivity increased to 11 emu/cm^3, 2 emu/cm^3, and 0.5 kOe, respectively. This phenomenon can be explained by the ferromagnetic component of $BiFeO_3$ induced by the parasitic ferromagnetic ordering at low temperature.

Figure 6 shows field cooling (FC) and zero field cooling (ZFC) curves of $BiFeO_3$ film. The applied magnetic field was 0.2 kOe. A broad peak was observed at around 70 K in the ZFC curve. The broad peak is not attributed to the magnetic transition because the Néel temperature of the $BiFeO_3$ is 653 K.[3] The melting temperature of Bi (T_m=541 K) is lower than that of Fe (T_m=1806 K), so that the small amount of Bi might be sublimated during the annealing process.[10] Therefore, the present $BiFeO_3$ film has the possibility of being an iron-rich $BiFeO_3$ film, which leads to the formation of the iron oxide nanoparticles or the distribution of the iron atoms in the $BiFeO_3$ film. Thus, the cause of the increment of the magnetic coercivity at 10 K might be considered to be not only the parasitic ferromagnetic ordering but also the superparamagnetic nanoparticles. When we assumed the existence of spherical magnetite nanoparticles in the superparamagnetic size with no internal magnetic interaction, the diameter was about 26 nm using the typical equation of the thermal fluctuation for the superparamagnetic nanoparticle (VK_u =25 k_BT, V, K_u, k_B, and T stand for magnetic volume, uniaxial magnetocrystalline anisotropy energy, Boltzmann's constant, and absolute temperature, respectively. K_u of bulk magnetite is around -11 kJ/m^3).[11] However, it is difficult to detect the existence of such small nanoparticles using conventional x-ray diffraction analysis, and therefore the transmission electron microscopy (TEM) observation is necessary to understand the origin of the peak in ZFC curve.

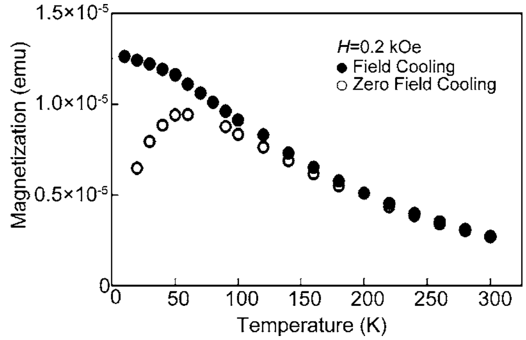

FIG. 6. FC-ZFC curves for the $BiFeO_3$ film with application of a magnetic field of 200 Oe. A broad peak was observed at around 70 K.

IV. CONCLUSION

We investigated the magnetic and the ferroelectric properties of multiferroic $BiFeO_3$ film prepared by CSD. The polycrystalline structure of the $BiFeO_3$ film was confirmed by examining x-ray diffraction patterns. The $BiFeO_3$ film showed the high remanent polarization of 47 μC/cm^2 at room temperature. The leakage current mechanism of the present $BiFeO_3$ film could be considered as follows: Ohmic conduction at low electric field and Poole-Frenkel trap limited conduction appeared as the electric field increased, and SCLC starts at a high electric field. The magnetic hysteresis loop at room temperature showed weak ferromagnetism and parasitic ferromagnetic ordering appeared as the temperature dropped to 10 K. However, according to the FC-ZFC measurement, the observed magnetic coercivity at 10 K may also be considered to be superparamagnetism.

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