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Ferroelectric and Magnetic Properties of Multiferroic BiFeO₃-Based Composite Films

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Abstract—BiFeO₃-based composite films were fabricated onto the Pt/Ti/SiO₂/Si(100) substrates by a chemical solution deposition (CSD) method using the precursor solutions with various excess iron composition followed by annealing at 923 K for 30 minutes under oxygen gas flow. Coexistence of spontaneous magnetization and remanent polarization could be obtained in the BiFeO₃-based composite films with high excess iron composition. The remanent magnetization of almost 20 emu/cm³ and the magnetic coercive field of 1.5 kOe were obtained at the iron composition ratio of Fe/Bi = 1.25. In this specimen, the remanent polarization at 90 K was approximately 10 μC/cm² at the electric field of 1500 kV/cm. Structural analysis suggested that the remanent polarization has a possibility to increase by suppressing the formation of the secondary phases of Bi₂Fe₄O₉ and α-Fe₂O₃, these are the nonferroelectric material as well as antiferromagnetic phase.

I. INTRODUCTION

MULTIFERROIC materials have coupled electric, magnetic, and structural order parameters that result in a simultaneous appearance of ferroelectricity, ferromagnetism, and ferroelasticity. One of the multiferroic materials, BiFeO₃ has attracted much interest because of the high remanent polarization of ~100 μC/cm² [1] as well as the high ferroelectric Curie temperature (T_C) of 1123 K [2]. On the contrary, although the BiFeO₃ material has a high Néel temperature of 653 K [3], [4], the high spontaneous magnetization as well as magnetic coercive field cannot be obtained, and the saturation magnetization is low [5], [6]. This is because of the G -type of the antiferromagnetism with the small spin canting system.

Recently, the multiferroic films of the ferroelectric-ferromagnetic composite-type have been reported, for example BaTiO₃-CoFeO₄ films showed the ferromagnetic properties together with the remanent polarization below 10 μC/cm² [7]. The (1- x)Bi₂Fe₄O₉- x BaO composites

($x = 0, 0.1, 0.2,$ and 0.3) films also showed the ferroelectricity together with the ferromagnetic properties [8]. The composite type of the multiferroic materials is one of the ways to achieve the coexistence of the ferroic properties at room temperature. In the present study, we fabricated the multiferroic BiFeO₃-based composite films by a chemical solution deposition (CSD) using the precursor solutions with various excess iron compositions and evaluated their magnetic properties as well as the ferroelectric properties.

II. EXPERIMENTAL PROCEDURE

BiFeO₃-based composite films were fabricated by the CSD method onto Pt/Ti/SiO₂/Si(100) substrates. The various Fe/Bi ratio of the precursor solutions were prepared by mixing the BiFeO₃ and the Fe₂O₃ precursor solutions with approximate ratios. The bottom and top Pt electrodes were deposited by an RF magnetron sputtering and an electron beam evaporation, respectively. A postdeposition annealing was carried out at 923 K for 30 minutes under the oxygen flow (flow rate: 80 ml/minute). The film thickness of the specimens was about 150 nm. The crystal structure was determined by a conventional x-ray diffraction (XRD: $2\theta/\theta$, Cu-K α ; PANalytical X'Pert MRD). The magnetic properties were measured by a vibrating sample magnetometer (VSM: TM-VSM261483-HGC) at room temperature with the maximum applied magnetic field of ± 18 kOe in the in-plane direction. The ferroelectric hysteresis loops at 90 K was measured by a ferroelectric tester (aixACCT TF-2000) with a single triangular pulse of 2 kHz. The positive-up, negative-down (PUND) measurements were carried out by a ferroelectric tester (aixACCT TF-2000) at 90 K and room temperature.

III. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns for Fe-rich BiFeO₃ films followed by the postdeposition annealing at 923 K for 30 minutes under the oxygen gas flow. Not only BiFeO₃ phase (●) but also α-Fe₂O₃ phase (□) and Bi₂Fe₄O₉ phase (○) were formed by adding the excess iron. The Bi₂Fe₄O₉ phase is the so-called pyrochlore phase, which does not show the ferroelectricity due to the inversion symmetry structure [8]. The Bi₂Fe₄O₉ is paramagnetism at room temperature due to antiferromagnetism with the Néel temperature of 265 K [9]. The α-Fe₂O₃ formed at high excess

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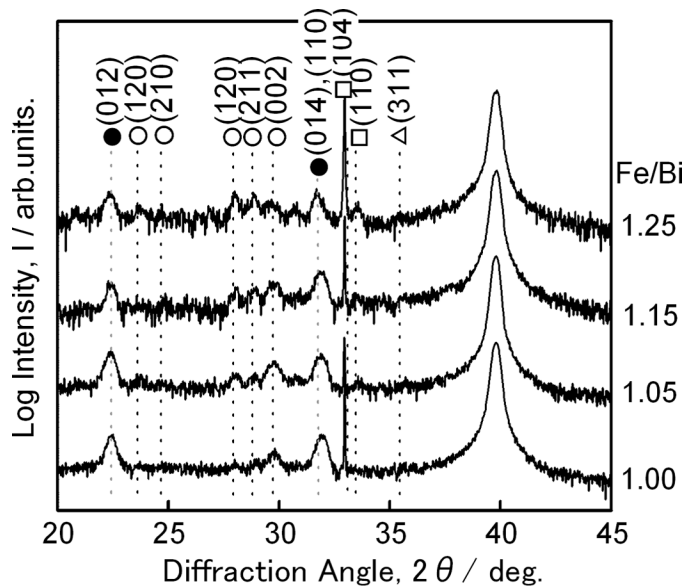


Fig. 1. X-ray diffraction patterns for Fe-rich BiFeO_3 films followed by the postdeposition annealing at 923 K for 30 minutes under the oxygen gas flow. (●) BiFeO_3 , (□) $\alpha\text{-Fe}_2\text{O}_3$, (○) $\text{Bi}_2\text{Fe}_4\text{O}_9$, and (△) Fe_3O_4 .

iron composition is antiferromagnetism ($T_N = 950$ K) together with the spin canting system. Therefore, the spin structure of the $\alpha\text{-Fe}_2\text{O}_3$ is almost the same as the BiFeO_3 . The weak diffraction peak due to (▽) Fe_3O_4 (311) was observed at the iron composition of $\text{Fe}/\text{Bi} = 1.25$. Fe_3O_4 is the ferromagnetic phase having Curie temperature beyond the room temperature.

Fig. 2 shows the atomic force microscopy (AFM) images for the BiFeO_3 films with various excess iron compositions. The grains of several hundred nanometer could be observed for the BiFeO_3 film ($\text{Fe}/\text{Bi} = 1.00$). The grain size as well as the surface morphology was not changed until the iron composition ratio of $\text{Fe}/\text{Bi} = 1.10$. At the iron composition ratio of $\text{Fe}/\text{Bi} = 1.2$ and 1.3 , grain size became smaller compared to the low excess iron composition. At Fe/Bi of 1.2 and 1.3 , several holes could be observed on the surface of the film, and the grains located around the holes seem to be twisted shape and relatively small grain size.

Fig. 3 shows the magnetic curves of the BiFeO_3 films with various excess iron compositions. The saturation magnetization also increased as the excess iron composition increased. The remanent magnetization and the magnetic coercive field are summarized in Fig. 4. The remanent magnetization and the magnetic coercive field increased with increasing the excess iron composition. The maximum remanent magnetization and the magnetic coercive field of about $20 \text{ emu}/\text{cm}^3$ and 1.5 kOe were obtained at the iron composition ratio of $\text{Fe}/\text{Bi} = 1.25$. The reason for the appearance of the spontaneous magnetization at high excess iron composition might be attributed to the formation of the secondary phase of the Fe_3O_4 because $\alpha\text{-Fe}_2\text{O}_3$ and $\text{Bi}_2\text{Fe}_4\text{O}_9$ phases are the antiferromagnetic materials. However, the diffraction peaks due to the Fe_3O_4 was too

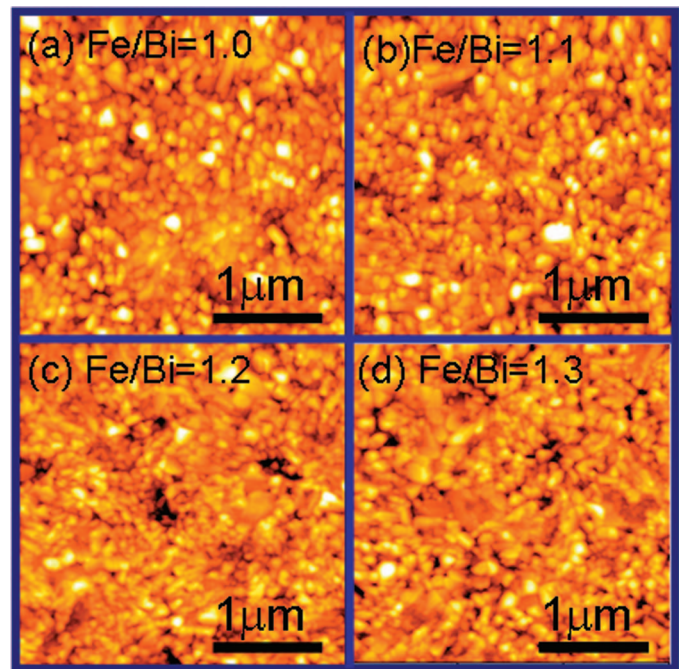


Fig. 2. AFM images for the BiFeO_3 films as a function of the excess iron composition.

TABLE I
LEAKAGE CURRENT DENSITY AT ROOM TEMPERATURE AND 90 K OF
THE VARIOUS EXCESS IRON COMPOSITION.¹

Fe/Bi	E (kV/cm)	r. t. (A/cm^2)	90 K (A/cm^2)
1.0	420	6.8	0.0017
1.1	470	1.0	0.0012
1.2	470	1.4	0.026
1.3	470	0.05	0.0004

¹The leakage current density was measured at the electric field at about $500 \text{ kV}/\text{cm}$ evaluated by the pulse form of the PUND measurements.

weak in the XRD patterns as shown in Fig. 1. Thus, the detail of the structural analysis by a transmission electron microscopy (TEM) observation is necessary to figure out the appearance of the spontaneous magnetization.

The leakage current density at the applied electric field of about $500 \text{ kV}/\text{cm}$ at room temperature and 90 K are summarized in Table I. The leakage current density was too high to measure the ferroelectric hysteresis loops at room temperature. The leakage current density drastically decreased by decreasing the measuring temperature. However, the influence of the leakage current density on the remanent polarization is unclear even at 90 K.

In order to clarify the influence of the leakage current component on the remanent polarization at 90 K, time dependence of the current was measured at 90 K using the PUND measurement system. Fig. 5 shows the magnified image of the response of the positive current against the trapezoid wave pulse measured at 90 K. In the BiFeO_3 film ($\text{Fe}/\text{Bi} = 1.00$), the current increased with increasing

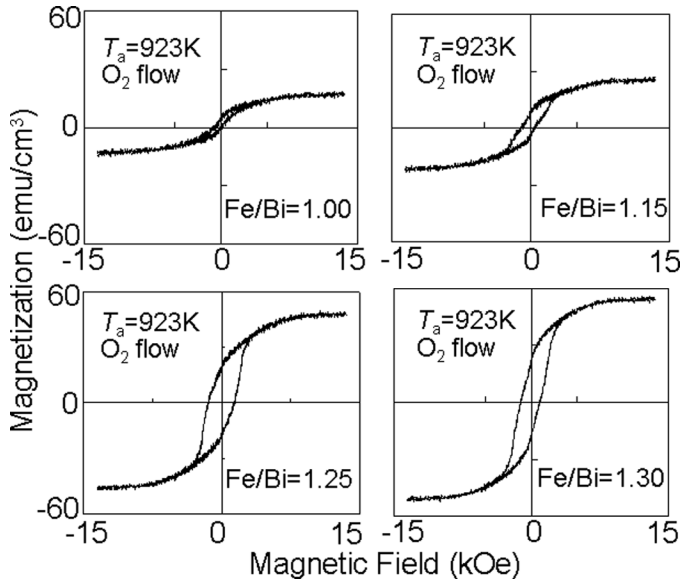


Fig. 3. Magnetic curves for the various excess iron compositions of the BiFeO_3 films.

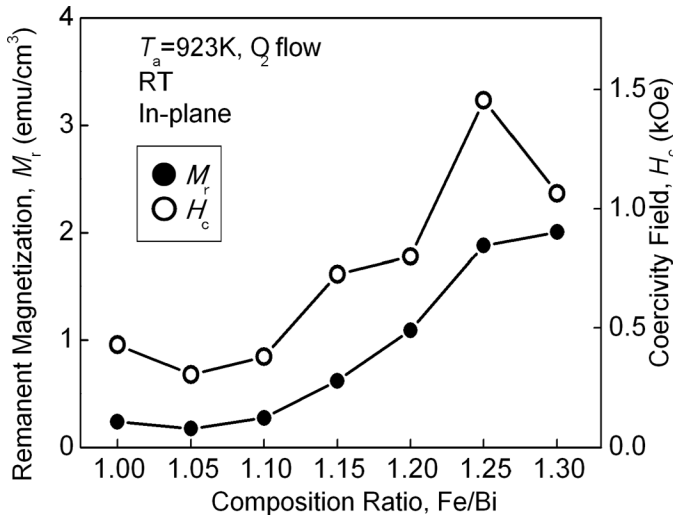


Fig. 4. Excess iron composition dependence of remanence magnetization and the magnetic coercive field.

the applied voltage, which is attributed to the inversion current due to the polarization. The inversion current decreased with increasing the excess iron composition. At the constant voltage region, the current drastically decreased, although the small current was still measured at the constant electric field region, which is attributed to the leakage current component. It was clearly shown that the leakage current component was much smaller than that of the inversion current. Therefore, it could be considered that the leakage current density does not strongly affect the polarization component.

Fig. 6 shows the ferroelectric hysteresis loops of the BiFeO_3 films with various excess iron compositions. The ferroelectric hysteresis loop of the BiFeO_3 film ($\text{Fe}/\text{Bi} = 1.0$) showed the remanent polarization of approximately $50 \mu\text{C}/\text{cm}^2$ together with the coercive field of ap-

proximately $500 \text{ kV}/\text{cm}$. When increasing the iron composition to $\text{Fe}/\text{Bi} = 1.1$, the remanent polarization drastically decreased although the coercive field of about $500 \text{ kV}/\text{cm}$ still remained. The ferroelectricity was observed until the composition of $\text{Fe}/\text{Bi} = 1.25$ and almost disappeared at $\text{Fe}/\text{Bi} = 1.30$. As mentioned above, the leakage current density does not affect the polarization component at 90 K , which indicates that the remanent polarization was intrinsically degraded by increasing the excess iron composition. Those results are consistent with the reduction of the inversion current as shown in Fig. 5. The degradation of the remanent polarization is attributed to the formation of the secondary phases of $\text{Bi}_2\text{Fe}_4\text{O}_9$, $\alpha\text{-Fe}_2\text{O}_3$, and Fe_3O_4 having inversion symmetry structure. Both $\text{Bi}_2\text{Fe}_4\text{O}_9$ and $\alpha\text{-Fe}_2\text{O}_3$ phases do not contribute to the enhancement of the spontaneous magnetization and remanent polarization. Therefore, these two secondary phases should be suppressed in the formation. On the contrary, Fe_3O_4 of the ferromagnetic phase should be formed in order to induce the spontaneous magnetization. It was suggested that a small amount of Fe_3O_4 embedded in the BiFeO_3 matrix is one way to realize the coexistence of the ferromagnetic and the ferroelectric materials in the BiFeO_3 -based composite films using the CSD process.

IV. CONCLUSIONS

We fabricated the BiFeO_3 -based composite films by the CSD method using the precursor solution with various excess iron compositions followed by post-deposition annealing at 923 K for 30 minutes under the oxygen flow, and we investigated the magnetic properties as well as the ferroelectric properties. The XRD measurements revealed that $\alpha\text{-Fe}_2\text{O}_3$, $\text{Bi}_2\text{Fe}_4\text{O}_9$ and Fe_3O_4 phases were formed at high excess iron composition. The appearance of the spontaneous magnetization might be attributed to the Fe_3O_4 of ferromagnetic phase although the formation of the Fe_3O_4 was difficult to identify in the XRD pattern. Therefore, further investigation using the TEM observation is necessary to confirm the existence of the Fe_3O_4 . The maximum remanent magnetization and the magnetic coercive field of approximately $20 \text{ emu}/\text{cm}^3$ and 1.5 kOe could be obtained at the iron composition of $\text{Fe}/\text{Bi} = 1.25$. On the contrary, the ferroelectric properties degraded by increasing the excess iron composition due to the formation of the secondary phases of $\text{Bi}_2\text{Fe}_4\text{O}_9$ and $\alpha\text{-Fe}_2\text{O}_3$. It was suggested that a small amount of Fe_3O_4 embedded in BiFeO_3 matrix is one way to realize the coexistence of the ferromagnetic and the ferroelectric materials in the BiFeO_3 -based composite films using the CSD process.

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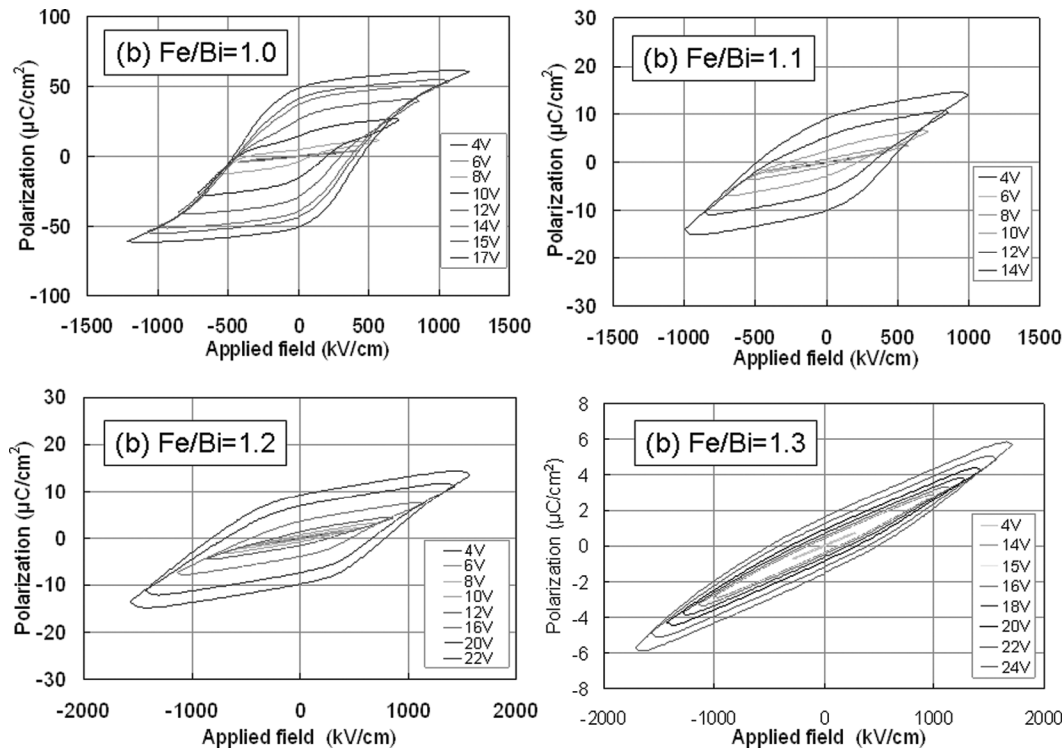


Fig. 5. Typical ferroelectric hysteresis loops measured at 90 K for the Fe-rich BiFeO_3 films.

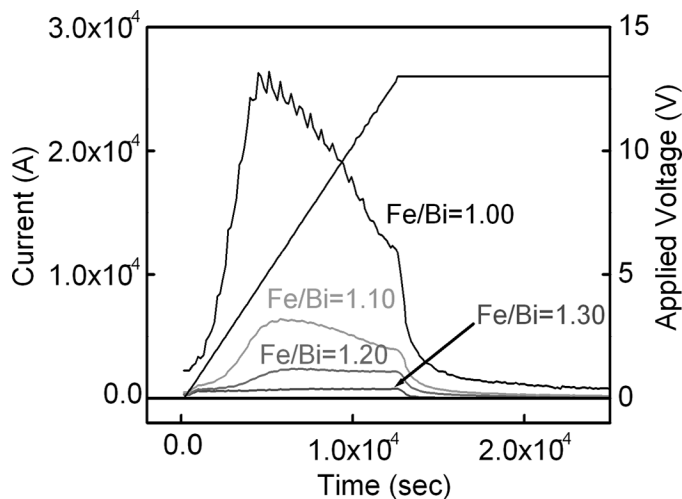


Fig. 6. Time dependence of the current in PUND measurements at 90 K for various excess iron composition.

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