Basic Study of Electric Field Induced Magnetization Reversal of Multiferroic (Bi$_{1-x}$Ba$_x$)FeO$_3$ Thin Films at Room Temperature for Magnetic Recording Technology

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(Bi$_{1-x}$Ba$_x$)FeO$_3$ multiferroic thin films with ferromagnetism and ferroelectricity were fabricated and applied to create magnetic recordings using an electric field. The (001)-oriented (Bi$_{1-x}$Ba$_x$)FeO$_3$ thin films of which electric polarization direction is perpendicular to the film plane were fabricated onto a non-single-crystalline substrate with a Ta seedlayer / (111)-oriented Pt underlayer at a low substrate temperature of 500 $^\circ$C. A very high frequency plasma irradiation was applied during sputtering deposition of (Bi$_{1-x}$Ba$_x$)FeO$_3$ to accelerate the crystallization at the low substrate temperature. The fabricated (Bi$_{0.6}$Ba$_{0.4}$)FeO$_3$ film exhibited hysteresis curves indicating ferromagnetic and ferroelectric behavior. The saturation magnetization of the film was approximately 60 emu/cm$^3$ and the coercivity was approximately 2.5 kOe, respectively. Magnetic Force Microscopy analysis of the (Bi$_{0.6}$Ba$_{0.4}$)FeO$_3$ film confirmed that the magnetization was reversed by applying only a local electric field. The multiferroic film described here is expected to be useful for electric field-driven magnetic devices.

**Key words:** Multiferroic thin film, control of magnetization direction, application of local electric field

1. Introduction

Magnetic recording using an electric field is a promising technology for future recording devices due to its lower power consumption and ease of recording. For example, magnetic field writing in hard disk drives (HDDs) will gradually become more difficult due to increased magnetic field required as the switching field of the bits in order to prevent thermal agitation of the recording media. Recently, energy-assisted magnetic recording technologies for next-generation HDDs, such as thermally-assisted magnetic recording$^{13}$ and microwave-assisted magnetic recording$^{15}$, have been widely studied in order to decrease the switching field. However, energy-assisted magnetic recording devices consume a large amount of power and the structure of the magnetic field writing head is complex due to the additional elements (a plasmon antenna for thermally-assisted magnetic recording or a spin-torque oscillator for microwave-assisted magnetic recording).

On the other hand, electric field writing can be used for HDDs with multiferroic recording media. The power requirement for switching the magnetization direction by this process is very low, the structure of the writing head is simple (involving a needle-shaped conductive element), and a very high electric field can be easily applied to the multiferroic layer because it is thin.

Therefore, the control of magnetization using electric fields is now being widely studied and several techniques have been reported. (1) The magnetoelectric effect has been used on piezoelectric and magnetostrictive laminate composites$^{33}$ or multilayer structures$^{6}$. (2) An electric field can be used to control the magnetic anisotropy of a thin metallic magnetic layer in magnetic tunnel junctions with three layers: a thin metallic magnetic layer, a thin insulating layer, and a metallic magnetic layer$^{5,6}$. (3) $\alpha$-Cr$_2$O$_3$ has both dielectric and antiferromagnetic properties so a notable exchange interaction occurs between layers of $\alpha$-Cr$_2$O$_3$ and a ferromagnetic material at room temperature$^{7}$ and magnetization switching occurs in the ferromagnetic layer when an electric field is applied due to antiferromagnetic coupling$^{8}$. (4) BiFeO$_3$ is a multiferroic material with a high ferroelectric Curie temperature of 1120 K and a high antiferromagnetic Neel temperature of 640 K. Thus, magnetization switching occurs in ferromagnetic layers fabricated on BiFeO$_3$ layers when an electric field is applied at room temperature due to antiferromagnetic coupling$^{9,10,11}$. (5) (Dy,Tb)FeO$_3$ is a multiferroic material that exhibits ferromagnetism and ferroelectricity and undergoes magnetization switching when an electric field is applied$^{12}$.

However, there are problems associated with the application of these systems to magnetic devices. In system (1), rapid operation of magnetization is difficult to achieve due to the use of a mechanical strain on the piezoelectric and magnetostrictive materials. Thus, the application of this system to magnetic devices that require a high-speed operation and high durability will be difficult. In system (2), unique and accurate electric field frequencies and DC magnetic field of several hundred oersteds have to be applied to reverse the magnetization of the thin metallic magnetic layer. Moreover, effective reversal of the magnetization can only be achieved with very thin metallic magnetic layers due to the interface effect between the metallic magnetic layer and the insulating layer. As a result, the application of this system to magnetic devices that
require large magnetization switching and a low error rate without a magnetic field will be difficult. In system (3), the antiferromagnetic Neel temperature of $\alpha$-$\text{Cr}_2\text{O}_3$ is not high (307 K) and not only an electric field but also a magnetic field are needed for magnetization switching. Further, the magnetization reversal can only be achieved with a very thin metallic ferromagnetic layer due to interface effect between the $\alpha$-$\text{Cr}_2\text{O}_3$ and ferromagnetic layer. Therefore, the application of this system to magnetic devices that must withstand high temperatures and require large magnetization switching without a magnetic field will be difficult. In system (4), the exchange interaction between the BiFeO$_3$ and ferromagnetic layer is small so the application of this system to magnetic devices that encounter large external fields and thus require large magnetization switching will be difficult. In system (5), the magnetic Curie temperature of almost multiferroic materials are very low, making the application of this system to practical magnetic devices difficult.

Therefore, a new system that can undergo magnetic switching in a single phase with ferromagnetism and ferroelectricity and with a high Curie temperature is needed for the magnetic recording via electric field writing. Several suitable multiferroic materials with ferromagnetism and ferroelectricity at room temperature, such as (Bi$_{1-x}$Ba$_x$)FeO$_3$ and Bi(Fe$_{1-x}$Co$_x$)O$_3$ [14,15], have been reported. In this study, we propose a novel magnetic recording technology based on electric field writing with a (Bi$_{1-x}$Ba$_x$)FeO$_3$ thin film that can be used to develop new magnetic recording devices with low power consumption. In HDDs with multiferroic recording media, the proposed system offers low power consumption for writing, a simple structure for the writing head, and a very high electric field for writing. The standard fabrication method for multiferroic films is pulsed-laser deposition onto single-crystalline substrates at a high temperature of more than 600 °C [16,17]. However, this method is not suitable for device manufacturing. In this study, we fabricated (001)-oriented (Bi$_{1-x}$Ba$_x$)FeO$_3$ thin films onto non-single-crystalline substrates at a relatively low substrate temperature of less than 500°C by magnetron sputtering. The obtained thin film had electric polarization direction perpendicular to the film plane and was suitable for device applications. Moreover, we demonstrated the control of the magnetization direction on the micrometer scale by applying a local electric field on a scanning probe microscope (SPM) with a Co-Zr-Nb coated conductive tip.

2. Experimental Procedure

Three layers were deposited onto a thermally oxidized Si wafer using an ultra-high-vacuum (UHV) sputtering system: 5 nm Ta, 100 nm Pt, and 100 nm (Bi$_{1-x}$Ba$_x$)FeO$_3$, in which the Ba concentration, $x$, was varied to 0, 0.1, 0.2, and 0.4. The layers were deposited at room temperature, 300 °C, and 400 - 500 °C, respectively. The film thicknesses and the deposition temperatures for the Ta seedlayer and Pt underlayer were optimized to obtain strong (111) orientation in the Pt underlayer [18]. Very-high-frequency (VHF) (40.68 MHz) plasma irradiation with an electric power of 5 W was applied during the radio-frequency (RF) (13.56 MHz) sputter deposition of the (Bi$_{1-x}$Ba$_x$)FeO$_3$ film. VHF plasma irradiation with a low power density has previously been reported to accelerate the crystallization of the film [19]. The crystallographic orientations and the crystalline structures of the fabricated (Bi$_{1-x}$Ba$_x$)FeO$_3$ films were analyzed by X-ray diffraction (XRD). The surface morphology of the BiFeO$_3$ films was examined by SPM with a Si tip. The magnetization curves of (Bi$_{1-x}$Ba$_x$)FeO$_3$ films and the Curie temperature $T_c$ of the (Bi$_{1-x}$Ba$_x$)FeO$_3$ film were measured using a vibrating sample magnetometer (VSM) with application of a magnetic field perpendicular to the film surface. The ferroelectric hysteresis loops of the (Bi$_{1-x}$Ba$_x$)FeO$_3$ films were measured using a ferroelectric tester. The local electric field was applied to the (Bi$_{1-x}$Ba$_x$)FeO$_3$ film using an SPM with a conductive, magnetic Co-Zr-Nb tip. The electric and magnetic domain structures of the (Bi$_{1-x}$Ba$_x$)FeO$_3$ film were analyzed by electric force microscopy (EFM) and magnetic force microscopy (MFM), respectively, with a conductive, magnetic Co-Zr-Nb tip.

3. Results and Discussions

Fig. 1 shows the XRD profiles of Bi-Fe-O films fabricated with various sputtering conditions on a thermally oxidized Si substrate with a Ta/Pt layer (the XRD profile of Ta/Pt layer is also illustrated). The Pt underlayer was found to have a strong (111) orientation and the full width at half maximum of the rocking curve for the Pt(111) diffraction was 2.0 degrees. The Bi-Fe-O film fabricated on the (111)-oriented Pt underlayer at a substrate temperature of 400°C was found to have a (001) orientation. Moreover, the Bi-Fe-O film fabricated

![Fig. 1 XRD profiles of Ta seedlayer /Pt underlayer and Bi-Fe-O films on Ta/Pt layer fabricated with various sputtering conditions.](image)

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on a (111)-oriented Pt underlayer at a substrate temperature of 400 °C with a VHF plasma irradiation power of 5 W was found to exhibit a strong (001) diffraction peak. The atomic force microscopy (AFM) images of the Bi-Fe-O films are also shown in this figure. The grain size of the Bi-Fe-O film fabricated in the presence of VHF plasma irradiation was found to be larger than that of the Bi-Fe-O film fabricated in the absence of VHF plasma irradiation. These results indicate that the use of a highly-oriented (111) Pt underlayer and VHF plasma irradiation are the key to obtaining strong (001) orientation and crystal grain growth in BiFeO₃ thin films at a relatively low substrate temperature.

Fig. 2 depicts the dependence of the saturation magnetization \( M_s \) and electric polarization at 750 kV/cm \( P_{750kV/cm} \) on the Ba concentration in the (001)-oriented (BiₓBa₁₋ₓ)FeO₃ film fabricated on an amorphous Ta seedlayer on a highly (111)-oriented Pt underlayer in the presence of VHF plasma irradiation. The maximum electric field used to measure the electric polarization was 750 kV/cm due to the insulating destruction. The magnetization hysteresis curve (major loop) and the ferroelectric hysteresis curve (minor loop) of the (BiₓBa₁₋ₓ)FeO₃ \((x=0.4)\) film are also illustrated in this figure. As the Ba concentration is increased, \( M_s \) increased. Based on the clear hysteresis in the magnetization curve and ferroelectric loops of (BiₓBa₁₋ₓ)FeO₃ film, the \( M_s \) was found to be about 60 emu/cm³; this is approximately the same as that of (BiₓBa₁₋ₓ)FeO₃ films fabricated by pulsed laser deposition on single-crystalline substrates at a temperature above 600 °C. The coercivity \( H_c \) of the \((\text{Bi}_{0.6}\text{Ba}_{0.4})\text{FeO}_3\) film was about 2.5 kOe and the squareness ratio \( M_r/M_s \) was 0.6. Based on the minor loop of the magnetic hysteresis loop (not shown), the magnetization reversal is thought to be dominated by a nucleation process. The relationship between the magnetic and electric properties will be discussed in a future study because only the minor loop of the electric property was measured here.

Fig. 3 shows the temperature dependence of \( M_s \) and the magnetization curve obtained at a temperature of 250 °C for the \((\text{Bi}_{0.6}\text{Ba}_{0.4})\text{FeO}_3\) film. Clear hysteresis was observed and \( T_c \) was estimated to be approximately 400 °C, which is useful for application to practical magnetic devices.

Figs. 4 (a), (b), and (c) show topographic, EFM, and MFM images, respectively, of the \((\text{Bi}_{0.6}\text{Ba}_{0.4})\text{FeO}_3\) film prior to the application of a DC voltage to the film. The MFM images were captured with a Co-Zr-Nb magnetic tip that was magnetized to saturation at the end of the tip such that the magnetization direction would be perpendicular to the sample surface and the direction of the detected magnetic field from the sample would also be vertical to the sample surface. For the EFM imaging, the Pt underlayer was grounded and a DC voltage of ±6.5 V (±650 kV/cm) for the Co-Zr-Nb conductive tip. Because this DC electric field was smaller than the coercive electric field of the \((\text{Bi}_{0.6}\text{Ba}_{0.4})\text{FeO}_3\) film, as depicted in Fig. 2, polarization reversal did not occur during this imaging. The MFM image shows the demagnetized domain structure, and the EFM image shows similar domain structure.

While writing on the \((\text{Bi}_{0.6}\text{Ba}_{0.4})\text{FeO}_3\) film using a local electric field, the surrounding area (3 µm square region) was scanned by the Co-Zr-Nb conductive tip on which a DC voltage of ±6.5 V was applied and the center area (1 µm square region) was scanned by the Co-Zr-Nb conductive tip on which a DC voltage of -6.5 V was applied. The DC voltage of ±6.5 V (±650 kV/cm) for the local electric field used for writing was larger than the coercive electric field of the \((\text{Bi}_{0.6}\text{Ba}_{0.4})\text{FeO}_3\) film so it was sufficient to reverse the electric polarization direction of the film. Figs. 4 (d), (e), and (f) show topographic, EFM, and MFM images of the \((\text{Bi}_{0.6}\text{Ba}_{0.4})\text{FeO}_3\) film after a DC voltage of ±6.5 V was applied. In the EFM image obtained with a with the tip voltage of ±1.0 V, an attractive force between tip and sample was observed in the center of the ferroelectric
(a) topographic, (b) EFM, and (c) MFM images of (Bi$_{1-x}$Ba$_x$)FeO$_3$ film before applying DC voltage, and (d) topographic, (e) EFM, and (f) MFM images of that film after applying DC voltage.

domain structure, which indicates a positive electric charge in this area. Conversely, in the surrounding area, a repulsive force between tip and sample was seen in the ferroelectric domain structure, indicating a negative electric charge. In an EFM image obtained with a tip voltage of +1.0 V (not shown here), the attractive force and repulsive force in the center area and the surrounding area were reversed. These images show that clear micrometer-scale ferroelectric domains were formed upon application of the local electric field. In the MFM image obtained with the tip magnetized at the end, a repulsive force between the tip and the sample was observed in the center of the ferromagnetic domain structure, indicating that the magnetization direction in this area was upward from the film surface. In the surrounding area, an attractive force between the tip and the sample was observed in the ferromagnetic domain structure, indicating that the magnetization direction was downward toward film surface. In an MFM image obtained with a tip voltage of 0 V, the relationship between the attraction and repulsion in the center area and the surrounding area did not change regardless of both before and after EFM measurements with tip voltages of -1.0 V and +1.0 V. Therefore, it can be concluded that micrometer-scale magnetization reversal was achieved by applying a local electric field and that the directions of $P$ and $M$ are parallel. Thus, the proposed multiferroic films are expected to be useful in novel magnetic recording devices driven by electric field writing.

4. Conclusion

In this study, we fabricated (Bi$_{1-x}$Ba$_x$)FeO$_3$ multiferroic thin films and demonstrated local magnetization reversal by the application of an electric field. The Ta seedlayer on the (111)-oriented Pt underlayer enabled successful fabrication of (001)-oriented (Bi$_{1-x}$Ba$_x$)FeO$_3$ thin films with electric polarization perpendicular to the film plane on a non-single-crystalline substrate. Further, sputtering deposition with VHF plasma irradiation was found to facilitate the crystallization of the (Bi$_{1-x}$Ba$_x$)FeO$_3$ thin films at a relatively low substrate temperature (compared to the standard method) of 500°C. The (Bi$_{1-x}$Ba$_x$)FeO$_3$ film, in which the Ba concentration was optimized, was found to have a high saturation magnetization of about 60 emu/cm$^3$, a high coercivity of about 2.5 kOe, and a high Curie temperature of about 400°C. MFM images revealed that the magnetization direction in the (Bi$_{1-x}$Ba$_x$)FeO$_3$ film could be controlled on a micrometer scale by simply applying an electric field. Based on these results, the proposed multiferroic film is expected to be useful for applications in electric field-driven magnetic devices.

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