1. Introduction

Multiferroic materials simultaneously display ferroelectric and ferromagnetic properties in the same phase. In the 1960s to 1970s, these materials were first investigated to understand the magnetoelectric (ME) coupling effect. Recently, there is increased interest in multiferroic materials because of their potential applications in novel devices using the magnetoelectric coupling effect. Very few intrinsic multiferroic compounds such as HoMnO$_3$ and TbMn$_2$O$_5$ exist in nature or have been synthesized. Furthermore, these materials exhibit the ME coupling at low temperatures.

BiFeO$_3$ has attracted great attention because it is multiferroic well above room temperature. However, the small magnetization and narrow growth window of BiFeO$_3$ impede its use in practical applications. To enhance the magnetic and ferroelectric properties of BiFeO$_3$, chemical modification, and controlled stress through growth of heteroepitaxial films and variation in thickness have been attempted with varying degrees of success. In Bi-Fe-O, however, there are several phases of different structures, compositions, and electrical and magnetic properties which can co-exist. The presence of these phases can substantially affect the electrical and magnetic properties of the overall material. There has been a report on the coexistence of BiFeO$_3$ and $\alpha$-Fe$_2$O$_3$ phases in Bi-Fe-O films grown by pulsed laser deposition (PLD). We have recently reported on the coexistence of BiFeO$_3$ and Fe$_2$O$_3$ phases ($\alpha$ and $\gamma$) with a systematically varying degree of mixture controlled by the oxygen partial pressure during deposition. In the present work, we investigate the microstructural evolution in Bi-Fe-O films which form nanocomposites consisting of more than one phase when the thickness of the film is changed. We focus on characterization of the secondary phases and the effects of these phases on the relaxation of the lattice misfit strain and the magnetic properties of the overall films.

Figure 1a shows X-ray diffraction (XRD) spectra obtained from films of different thicknesses, $t$, grown at an oxygen partial pressure of 5 mTorr. Diffraction was performed using the $\omega$-scan mode, and the intensities were integrated in $\chi$ between 85 and 95 degrees. The corresponding TEM cross-sectional images of some of the films are shown in Figure 1b. In our previous report, thin films of pure BiFeO$_3$, which has a perv...
skite structure in bulk with $a = 0.395$ nm,[16] grown at 20 mTorr and higher oxygen partial pressure showed a monoclinically distorted (by about 0.5°) tetragonal structure with the lattice constants, $a = 0.394$ nm, $c = 0.398$ nm. In the present work, the 35 nm thick film grown at 5 mTorr oxygen partial pressure shows the pure epitaxial BiFeO$_3$ phase with the [001] orientation and a slightly larger lattice parameter ($c = 0.407$ nm) than that of the pure 300 nm thick BiFeO$_3$ film grown at 20 mTorr. As the film thickness increases, the intensity of the (002) diffraction peaks of the BiFeO$_3$ increases, and the peak shifts to a higher 2$\theta$ angle (see Fig. 1a). This indicates that the out-of-plane lattice parameters of BiFeO$_3$ decreases with increasing thickness. We also observed peaks corresponding to the (024) plane of the $\alpha$-Fe$_2$O$_3$ phase and the (240) plane of the $\gamma$-Fe$_2$O$_3$ phase. The $\alpha$-Fe$_2$O$_3$ phase has a rhombohedral crystal structure (space group: R-3c) with lattice constants of $a = b = 0.505$ nm, $c = 1.319$ nm, and the $\gamma$-Fe$_2$O$_3$ phase has the cubic (or inverse spinel) crystal structure that belongs to the space group P4132 (or Fd-3m) with lattice parameters $a = 0.83515$ nm.[17] The intensity of the peaks corresponding to $\alpha$- and $\gamma$-Fe$_2$O$_3$ in Figure 1a increases with increasing film thickness.

From the TEM cross-sectional images of films with different thickness shown in Figure 1b, we can see that the secondary phase, $\alpha$-Fe$_2$O$_3$, forms in the surface region of films with thickness of 50 nm, which grows to the surface of the film with continued deposition. The EDS spectra in Figure 1b obtained from the bright and dark columns of the film confirmed the chemical composition of the separated phases. The EDS spectrum from the bright columns shows little bismuth contents (5.5 at %), and the ratio between iron (38.5 at %) and oxygen (56 at %) is 1:1.45, which is consistent with Fe$_2$O$_3$. The EDS spectrum from the dark columns shows a 1:1.1 ratio between bismuth (24 at %) and iron (26.3 at %), which is consistent with BiFeO$_3$.

The magnified TEM images from cross-sectional and plan-view specimens in Figure 2a show that the $\gamma$-Fe$_2$O$_3$ phase forms precipitates with a plate-like shape embedded in the $\alpha$-Fe$_2$O$_3$ regions. From indexing the SAD patterns (see Fig. 2b), we obtained the following preferred in-plane epitaxial relations among BiFeO$_3$, $\alpha$-Fe$_2$O$_3$, and $\gamma$-Fe$_2$O$_3$: [100]$_{\text{BiFeO}_3}$/[100]$_{\alpha}$, [120]$_{\gamma}$/[120]$_{\alpha}$, and [010]$_{\text{BiFeO}_3}$/[11–1]$_{\alpha}$/[2–1–1]$_{\gamma}$. The $\gamma$-Fe$_2$O$_3$ also showed different orientations with respect to BiFeO$_3$ and $\alpha$-Fe$_2$O$_3$ in other areas of the sample. Typically, Fe$_2$O$_3$ has two different crystal structures. One is a spinel structure (magnetite, $\gamma$-Fe$_2$O$_3$) and the other is a corundum structure (hematite, $\alpha$-Fe$_2$O$_3$). In bulk, it is known that there is an irreversible transformation from $\gamma$-Fe$_2$O$_3$ to $\alpha$-Fe$_2$O$_3$ occurring at temperatures above 400 °C via restacking of the oxygen layers and displacement of the Fe ions located in the interstices rather than recrystallization.[18] This transformation occurs on the close-packed planes of $\alpha$- and $\gamma$-Fe$_2$O$_3$ without diffusion, and thus the crystal orientation relationship between $\alpha$- and $\gamma$-Fe$_2$O$_3$ in the bulk was reported as (0001)$_{\alpha}$/[111]$_{\gamma}$, [01–10]$_{\alpha}$/[1–10]$_{\gamma}$,[17,19,20] In our experiments, however, we observed the co-

Figure 1. a) X-ray diffraction spectra (in log scale) and b) TEM cross-sectional images (left) and EDS spectra (right) of Bi-Fe-O films grown at 5 mTorr with different thickness. Nucleation of impurity phases starts at ~50 nm. The intensity of the peak labeled Fe$_2$O$_3$ in (a) corresponding to the impurity phase increases with increasing film thickness.

Figure 2. TEM bright field images and SAD pattern of bismuth iron oxide thin films fabricated on (001) SrTiO$_3$ substrates. a) Cross-section (left) and plan-view (right) images showing $\gamma$-Fe$_2$O$_3$ precipitates and b) SAD pattern and corresponding schematic of $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$ phases in the film deposited at 1 mTorr. c) High resolution cross sectional TEM image of $\gamma$-Fe$_2$O$_3$ in $\alpha$-Fe$_2$O$_3$ matrix.
existence of $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$ in the film. Furthermore, the $\gamma$-Fe$_2$O$_3$ phase in the present study showed several different orientation relationships with $\alpha$-Fe$_2$O$_3$. This is probably due to the fact that PLD is a non-equilibrium growth technique.

The SAD pattern and the schematic in Figure 2b are from one of the Fe$_2$O$_3$ regions where $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$ coexist. The out-of-plane and the in-plane parameters of $\alpha$-Fe$_2$O$_3$ as measured from the SAD patterns were $d(102) = 0.364$ nm and $d(1\overline{1}2) = 0.370$ nm, respectively. The out-of-plane and the in-plane parameters in $\gamma$-Fe$_2$O$_3$ as measured from a high resolution TEM image (see Fig. 2c) were $d(120) = 0.37$ nm and $d(2\overline{1}1) = 0.34$ nm, respectively, which are in good agreement with published values (i.e., JCPDS #39-1346). The lattice mismatch between $\alpha$- and $\gamma$-Fe$_2$O$_3$ is 8.1%. A distortion of the $\alpha$-Fe$_2$O$_3$ lattice and strain concentration around $\gamma$-Fe$_2$O$_3$ was observed due to the large lattice mismatch.

The existence of secondary phases can affect the relaxation of misfit strain in BiFeO$_3$ and result in significant change in the ferroelectric and ferromagnetic properties of the BiFeO$_3$ film. To compare the relaxation mechanism of the out-of-plane lattice parameter of multiphase Bi-Fe-O with pure BiFeO$_3$, Bi-Fe-O films with a gradual change in thickness were fabricated by the gradient deposition technique using a shadow mask. An oxygen partial pressure of 20 mTorr was selected to fabricate a pure BiFeO$_3$ film with small thickness showed a highly strained film as expected. However, the thicker region of the film showed both a relaxed region (represented by the X-ray “peaks” labeled B in Figure 3b and a highly strained region (labeled A in Fig. 3b) in the film even though the thickness of the film was above the critical thickness for relaxation to take place. This observation can be explained by the formation of $\alpha$-Fe$_2$O$_3$ regions, which appeared in the surface region of the film with thickness $\geq 50$ nm. The transformation to $\alpha$-Fe$_2$O$_3$ in the surface region of the film reduces the thickness of the BiFeO$_3$ underneath. Therefore, the area below $\alpha$-Fe$_2$O$_3$ (marked A in Fig. 1b) showed higher misfit in-plane strain and a lower misfit dislocation density than the region with pure BiFeO$_3$ surrounding the $\alpha$-Fe$_2$O$_3$ columns (marked B in Fig. 1b) as determined by high resolution TEM images (not shown). The formation of $\alpha$-Fe$_2$O$_3$ regions enhances the relaxation of in-plane misfit strain in the BiFeO$_3$ columns between $\alpha$-Fe$_2$O$_3$ columns due to the reduction in volume (calculated below). The reduction of volume releases both the in-plane compressive strain and out-of-plane tensile strain in the BiFeO$_3$ regions surrounding $\alpha$-Fe$_2$O$_3$ (see Fig. 3d).

In order to determine if the strain relaxation mechanism of the multiphase film was due to the gradient in thickness, several multiphase Bi-Fe-O films, with constant thickness (35–500 nm), were grown and compared to the single phase BiFeO$_3$ film with a gradual change in thickness (see Fig. 4a).
change of out-of-plane lattice parameter with thickness was obtained from the pure BiFeO3 film with thickness gradient grown at 20 mTorr and the multiphase Bi-Fe-O films with constant thickness grown at 5 mTorr (see Fig. 4a). Both pure and multiphase films with 35 nm thickness showed a high degree of strain. As the film thickness increases from 30 to 300 nm, the out-of-plane lattice parameter of the pure BiFeO3 film gradually decreases from 0.406 to 0.398 nm. However, in the multiphase films, the out-of-plane lattice parameter decreases from 0.407 to 0.396 nm with increasing film thickness from 35 to 500 nm. This result confirms that the α-Fe2O3 domains that form on the surface region of the film for films of thickness above 50 nm (grown at low oxygen partial pressure) enhance the in-plane relaxation of misfit strain in the BiFeO3 columns. As a result, the total misfit strain reduction is from 0.51 % (pure BiFeO3) to 0.25 % (mixture of BiFeO3 and Fe2O3) at the thickness of ~300 nm. The observation of a broad peak in the XRD spectra in Figure 3b for thicknesses above ~50 nm indicates that the bottom portion of the films under the Fe2O3 region (region A) in Figure 1b remains strained. In order to understand the higher degree of strain relaxation in the films with Fe2O3, we estimate the change in volume in these regions. A reduction in volume of ~19% by the formation of the Fe2O3 phase allows expansion (in plane) of BiFeO3 (which is under in-plane compressive strain with the substrate). This in-plane expansion, together with the formation of the vertical boundary between BiFeO3 and Fe2O3, lowers the out-of-plane strain in the film. Therefore, the formation of α-Fe2O3 by evaporation of the more volatile Bi metal at relatively low oxygen partial pressure enhances the relaxation of the compressive stress in BiFeO3. The relaxation is accelerated as the α-Fe2O3 volume fraction increases.

The existence of secondary phases also affects the magnetic properties of the films. We recently reported the dependence of the magnetic properties on the formation of Fe2O3 phases as controlled by the oxygen partial pressure during growth of Bi-Fe-O films.[15] The saturation magnetization increased to about 80 emu cm−3 due to the increase in the volume fraction of γ-Fe2O3 in the film. In the present study, we compare the effect of strain and the formation of γ-Fe2O3 on the magnetization of BiFeO3 films. α-Fe2O3 and BiFeO3 are known as canted antiferromagnetic materials at room temperature, and they exhibit weak magnetization of 0.4 emu cm−3 and 2 emu cm−3 at room temperature, respectively.[21,22] In contrast, bulk γ-Fe2O3 is known to display magnetization of up to 400 emu cm−3 at room temperature.[23] In our previous study of BiFeO3 films, the increase in volume of the γ-Fe2O3 with increasing film thickness showed a great effect on the magnetic properties of the films grown at less than 5 mTorr oxygen pressure.[15] However, the films grown at 5 mTorr oxygen pressure did not show dramatic increase in magnetization due to a small amount of γ-Fe2O3. The magnetization in this sample was controlled by residual strain in the film. Figure 4b shows the change in magnetization with thickness for films grown at 5 mTorr and 20 mTorr oxygen partial pressures. Both pure BiFeO3 and multiphase Bi-Fe-O films exhibit higher magnetization for the thinner films than for thick films. From the XRD results in Figure 4a, the 35 nm thick film grown at 5 mTorr shows higher strain and higher magnetization (~5 emu cm−3) (Fig. 4b) than the 50 nm thick BiFeO3 film grown at 20 mTorr. However, the observed improvement of magnetization is still smaller than the results of Wang et al.[5] but it is in agreement with other recent measurements.[13] This enhanced magnetism could result from the heteroepitaxial strain effect in the canted antiferromagnetic film. The magnetic moments of Fe in BiFeO3 are ferromagnetically aligned on the (111) plane and antiferromagnetically switched along the [111] direction. Canting of Fe magnetic moment allows weak ferromagnetism in BiFeO3.[24,25] Ederer and Spaldin found through density functional theory calculations that weak ferromagnetic moments (0.1μB per unit cell for about 1° canting from the collinear direction) are induced by a structural distortion.[26]

The BiFeO3 in-plane lattice parameter, which is reduced by the compressive stress from the SrTiO3 substrate, results in elongation of the out-of-plane lattice parameter. This strain gives rise to enhancement of magnetization.[5,13] As the thickness increases, this strain is relaxed and the magnetization is expected to decrease. Since the multiphase BiFeO3 films have higher strain relaxation due to the formation of α-Fe2O3 domains, the magnetization in these films is expected to decrease faster than for pure BiFeO3 films with increasing thickness. However, this reduction of magnetization is partially compensated by the nucleation of γ-Fe2O3. The saturation magnetiza-
shows a columnar structure of BiFeO$_3$ and Fe$_2$O$_3$. Relatively film obtained using PFM at room temperature. Figure 6a magnetic domains in the films correspond to the Fe$_2$O$_3$ regions.

Comparing the MFM image in Figure 5d, we can see that the magnetic domains with zero field that switch in the perpendicular direction under an applied magnetic field is shown in Figure 5a. The annealed film showed increased magnetization (∼6 emu cm$^{-3}$) due to the increase of the γ-Fe$_2$O$_3$ fraction (less than 10%). The magnetic domain image of the annealed multiphase Bi-Fe-O film was acquired using MFM to confirm the existence of magnetic domains (γ-Fe$_2$O$_3$) after annealing. Figure 5b shows randomly oriented magnetic domains with zero field that switch in the perpendicular direction under an applied magnetic field (Fig. 5d). Comparing the AFM image in Figure 5c with the MFM image in Figure 5d, we can see that the magnetic domains in the films correspond to the Fe$_2$O$_3$ regions. From these results, we conclude that the magnetic properties of the films can be controlled by converting α-Fe$_2$O$_3$ into γ-Fe$_2$O$_3$ through the described procedure. In fact, we found that the magnetization of the films is directly proportional to the volume fraction of γ-Fe$_2$O$_3$ which can be controlled by adjusting the annealing time and the concentration of hydrogen in the gas mixture.

Also, effects of the Fe$_2$O$_3$ phase formation and microstructural change on the ferroelectric properties of BiFeO$_3$ films were studied using piezo force microscopy (PFM). Figure 6a and b show a topographic image and an out-of-plane piezoelectric response image, respectively, of a multiphase BiFeO$_3$ thin film obtained using PFM at room temperature. Figure 6a shows a columnar structure of BiFeO$_3$ and Fe$_2$O$_3$. Relatively high regions represent BiFeO$_3$. To obtain the piezoelectric response image, the multiphase BiFeO$_3$ film (Fig. 6b) and pure BiFeO$_3$ film (Fig. 6c) were first poled by applying a positive DC bias (+10 V) to a conducting probe while scanning over a $3 \times 3$ μm$^2$ area. Another poling was then performed with a negative voltage (−10 V) during a scan over a $1 \times 1$ μm$^2$ area. The PFM image shows both written regions with opposite contrast because of the presence of switching of ferroelectric domains in the film. Comparing switching of domains in the pure BiFeO$_3$ film (Fig. 6c) to the multiphase BiFeO$_3$ film (Fig. 6b), the multiphase BiFeO$_3$ film shows enhanced piezoelectric response with higher contrast of switching in polarization in the interfacial regions between BiFeO$_3$ and Fe$_2$O$_3$ than the pure BiFeO$_3$ film. This result is surprising because Fe$_2$O$_3$ is not ferroelectric. It is possible that local strains and/or composition gradients across these interfacial regions are responsible for the enhanced piezoelectric response. These possibilities are currently under further investigation.

In conclusion, pure BiFeO$_3$ films were grown on SrTiO$_3$ with 20 mTorr oxygen pressure. At oxygen pressures below or equal to 5 mTorr, regions containing α-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$ appear on the top region of the film when the thickness of the film is ∼50 nm. With continuous deposition, these Fe$_2$O$_3$ regions continue to grow to the surface of the film. γ-Fe$_2$O$_3$ nucleates in α-Fe$_2$O$_3$ with specific orientation forming plate-like structures. The distribution of misfit strain in multiphase Bi-Fe-O film was
Bi-Fe-O thin films with constant thickness (35–500 nm) and with a thickness gradient were deposited on SrTiO3 (001) substrates at a temperature of 650 °C by PLD. We ablated a stoichiometric BiFeO3 target with a KrF excimer laser (λ = 248 nm) with a typical fluence of 2 J cm−2. The substrates were preheated to 650 °C before deposition, and the deposition rate was 6 nm min−1. To investigate the multiphase formation, the oxygen partial pressure was varied in the range of 0.1 to 20 mTorr. We also examined the evolution of the crystal structure in films as a function of thickness ranging from 35 to 500 nm, all grown at a constant oxygen partial pressure (5 mTorr). Scanning X-ray microdiffraction (using a D8 DISCOVER with GADDS for combinatorial screening) and EDAX energy dispersive X-ray spectroscopy (EDS) in a JEOL 2010F field emission transmission electron microscope (TEM) were used for identifying the secondary phases. The structural properties of the films were studied by TEM, TEM images and selected area diffraction (SAD) patterns of the films were obtained with a JEOL 4000-FX TEM operated at an accelerating voltage of 300 kV and a JEOL 2100F field emission TEM operated at an accelerating voltage of 200 kV. A MPMS-5 superconducting quantum interference device (SQUID) magnetometer and Digital Instruments (DI) Dimensions 3000 magnetic force microscopy (MFM) were used to perform magnetic characterization. PFM was performed in contact mode on BiFeO3/Nb-doped SrTiO3 structures using Pt-Ir coated tips [28].