Microstructure and phase control in Bi−Fe−O multiferroic nanocomposite thin films

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We report on the controlled multiphase thin film growth in the Bi−Fe−O system. By varying the deposition oxygen pressure, the dominant phase formed in the film continuously changes from ferroelectric $BiFeO_3$ to a mixture of α-Fe_2O_3 and ferromagnetic γ-Fe_2O_3. X-ray diffraction and high-resolution transmission electron microscopy have revealed that epitaxial multiferroic nanocomposites consisting of $BiFeO_3$ and Fe_2O_3 are formed when the deposition pressure is ≈ 5 mTorr. In order to investigate the previously reported anomalous enhancement in magnetization in $BiFeO_3$, we have fabricated a thickness gradient pure $BiFeO_3$ film. The out-of-plane lattice constant was found to increase continuously as the thickness is decreased from 300 to 5 nm, but no significant enhancement in magnetization was observed. © *2006 American Institute of Physics.*
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Recently, $BiFeO_3$ has attracted much attention.[1,2] There have been a number of reports on thin film $BiFeO_3$, but their multiferroic properties have not been unambiguously established.[3,4] Recently, Béa *et al.* have reported on the parasitic phases in $BiFeO_3$ thin films.[5] However, detailed study of the microstructure of the films was not presented. In this study, we report on the microstructural properties of multiphase bismuth iron oxide thin films using transmission electron microscopy (TEM). Coexisting $BiFeO_3$ and Fe_2O_3 phases (α and γ) are observed in the films with a systematically varying degree of mixture controlled by the deposition oxygen partial pressure. The columnar epitaxial mixture of ferroelectric $BiFeO_3$ and Fe_2O_3 represents a new type of multiferroic nanocomposite material.

In order to fabricate bismuth iron oxide thin films by pulsed laser deposition, we ablated a stoichiometric $BiFeO_3$ target with a KrF excimer laser ($\lambda = 248$ nm) with a typical fluence of 2 J/cm^2. The oxygen pressure and the substrate temperature during the deposition were varied in the ranges of 0.025–100 mTorr and 550–750 °C, respectively. The typical deposition rate was 5 nm/min, and $SrTiO_3$ (STO) (001) was used as the substrate. Scanning x-ray microdiffraction (using a D8 DISCOVER with GADDS for combinatorial screening by Bruker-AXS) and TEM were used for structural characterization of the films. TEM images and selected area diffraction (SAD) patterns of the films were obtained at an accelerating voltage of 300 keV using a JEOL 4000-FX

TEM. A superconducting quantum interference device (SQUID) magnetometer and a low temperature scanning SQUID microscope were used to perform magnetic characterization.

Figure 1 shows x-ray diffraction (XRD) spectra of the 300 nm thick bismuth iron oxide thin films deposited under different oxygen pressures. Diffraction was performed using the ω-scan mode, and the intensities were integrated in χ between 85° and 95°. Epitaxial $BiFeO_3$ films with the [001] axis perpendicular to the substrate surface were obtained at oxygen pressure higher than 1 mTorr, and the intensity of the (002) diffraction peaks of the $BiFeO_3$ increases as the
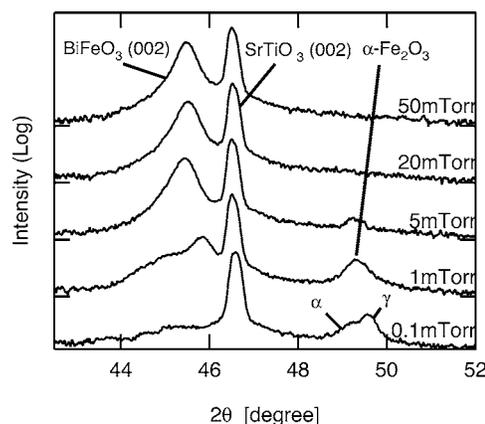
FIG. 1. (Color online) X-ray diffraction (in log scale) of bismuth iron oxide thin films deposited under different oxygen partial pressures.

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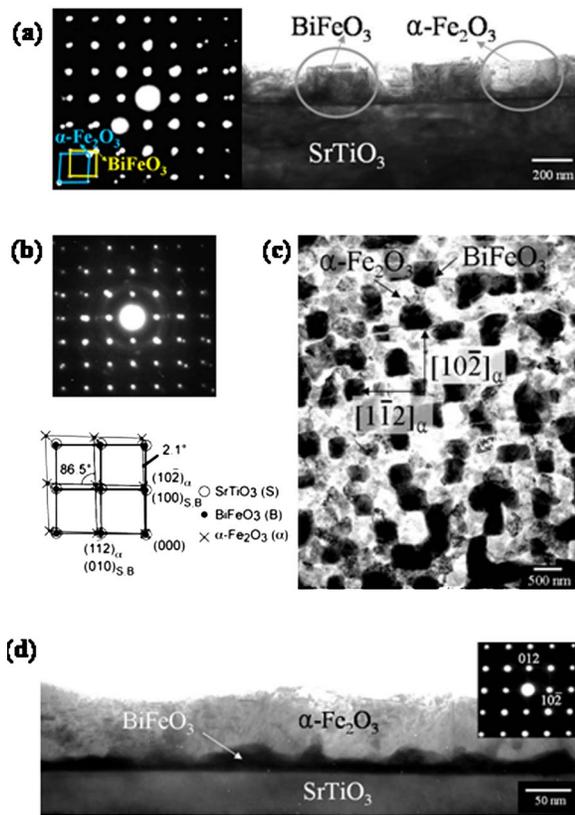
FIG. 2. (Color online) TEM bright field images and SAD patterns of bismuth iron oxide thin films fabricated on (001) $SrTiO_3$ substrates: (a) cross-sectional image and SAD pattern of the film deposited at 1 mTorr; (b) plan view SAD pattern with schematic; (c) plan view image of the same film as (b) deposited at 1 mTorr; and (d) cross-sectional image and corresponding SAD pattern of a film deposited at 0.1 mTorr.

pressure increases. Bi_2O_3 phase was also observed at oxygen pressure higher than 50 mTorr.[5] We also observe peaks corresponding to the α-Fe_2O_3 phase with the [012] orientation when the oxygen pressure is less than 5 mTorr, and the intensity of these peaks increases as the oxygen pressure decreases. A mixture of $BiFeO_3$ and α-Fe_2O_3 phases was observed for the deposition pressure between 1 and 5 mTorr. This transition in the dominant phase in the film reflects the change in the amount of the Bi incorporation in the films due to the high volatility of Bi metal. As we decrease the deposition oxygen pressure, the Bi content in the films decreases. When the deposition pressure is less than 1 mTorr, we also see a peak from γ-Fe_2O_3. At the oxygen pressure of 20 mTorr, the film is single phase $BiFeO_3$, and it shows a monoclinically distorted (by about 0.5°) tetragonal structure. The lattice constants of the $BiFeO_3$ calculated from electron diffraction data (not shown) are $a=0.394$ nm, $c=0.398$ nm. The films are relaxed at a thickness of 300 nm, and these lattice parameters agree with ones reported by others.[2,6] We do not observe any impurity phases in films deposited under this condition. We believe the shift in the (002) diffraction at 1 mTorr is caused by relaxation of $BiFeO_3$ resulting from stabilization of the phase separated configuration of $BiFeO_3$ and Fe_2O_3 phases. The smaller broad (002) peak corresponding to a larger lattice constant is likely from the thin layer of strained $BiFeO_3$ at the substrate interface discussed below.

Figure 2 shows TEM images of 200 nm thick bismuth iron oxide thin films. $BiFeO_3$ and Fe_2O_3 phases were found to have grown epitaxially with respect to the substrate as

well as with respect to each other in the lateral direction in a columnar manner. We have found that the Fe_2O_3 domains grow with a mixture of α and γ phases, with α being the predominant phase. Fig. 2(a) is a cross-sectional bright field image of the film showing the presence of $BiFeO_3$ and α-Fe_2O_3. This film was grown at 1 mTorr of oxygen. The corresponding SAD pattern from the α-Fe_2O_3 was identified as the superposition of the (100) pattern from $BiFeO_3$ and that of the rhombohedral crystal structure of α-Fe_2O_3 (space group: $R\bar{3}c$) with lattice constants of $a=b=0.505$ nm, $c=1.319$ nm, which are in good agreement with the published structure (i.e., JCPDS No. 33-0664). We have also confirmed this result with energy dispersive x-ray spectroscopy. The epitaxial relationship of $BiFeO_3$ and α-Fe_2O_3 was determined from the electron diffraction patterns of the cross-sectional view [inset of Fig. 2(a)] and the plan view [Fig. 2(b)]: $[001]_{BiFeO_3}$ is seen to be almost parallel (within 0.2°) to $[001]_{STO}$ (corresponding to the out-of-plane direction). However, [012] of α-Fe_2O_3 is deviated by 2.1° from $[001]_{BiFeO_3}$. Figure 2(c) is a plan view TEM image taken from the same sample grown at 1 mTorr. The interface between $BiFeO_3$ and α-Fe_2O_3 is parallel to the $[10\bar{2}]$ and $[1\bar{1}2]$ directions of α-Fe_2O_3. From the electron diffraction patterns, $[100]_{BiFeO_3}$ is seen to be almost parallel to $[100]_{STO}$ (corresponding to the in-plane direction), with the in-plane lattice parameters of 0.394 and 0.3905 nm, respectively. However, $[10\bar{2}]$ of α-Fe_2O_3 makes an angle of ~2.1° with respect to the $[100]_{BiFeO_3}$. The measured interplanar distance between (000) and $(10\bar{2})$ of α-Fe_2O_3 is 0.370 nm, which is slightly larger than a published result (0.3684 nm, JCPDS No. 33-0664) for bulk α-Fe_2O_3. These results can be explained as a consequence of an in-plane tensile stress imposed by $BiFeO_3$ on the α-Fe_2O_3. The increase of the $(10\bar{2})$ interplanar distance gives rise to a decrease in the (012) interplanar distance, which was measured as 0.364 nm. The lattice mismatch strain between $BiFeO_3$ and α-Fe_2O_3 is 7.1%. After relaxation, a residual strain of 5.9% was calculated from our TEM and XRD results. Fig. 2(d) shows a bismuth iron oxide thin film fabricated at 0.1 mTorr. At this low pressure, the dominant phase is α-Fe_2O_3 which forms a continuous layer on a thin layer (≈ 5 nm) of $BiFeO_3$ above the substrate. The fact that α-Fe_2O_3 appears to have grown above $BiFeO_3$ indicates that it nucleated at the top surface of the film as Bi atoms vaporized following deposition. In a recent letter,[5] a mixture of $BiFeO_3$ and γ-Fe_2O_3 (maghemite) grown at low oxygen partial pressure was reported. Their XRD results and magnetic properties are consistent with the second phase being γ-Fe_2O_3. However, in our experiments, the dominant phase at low oxygen partial pressure was revealed to be α-Fe_2O_3 from the TEM analysis. The SAD pattern in the inset of Fig. 2(d) taken from the iron oxide area was indexed to α-Fe_2O_3 and the measured angle (~86.5°) between (012) and $(10\bar{2})$ agrees well with the calculated angle (86.0°) in rhombohedral bulk α-Fe_2O_3. However, we also found a small trace of γ phase precipitates with a plate-like shape embedded in the α-phase matrix. Indeed, in XRD in Fig. 1, a peak from γ-Fe_2O_3 is located fairly close to that of α-Fe_2O_3. We have not studied the influence of temperature on the nanostructure of the films in detail, but we expect similar trends in structure changes when either the oxygen partial pressure is decreased or the deposition temperature is in-
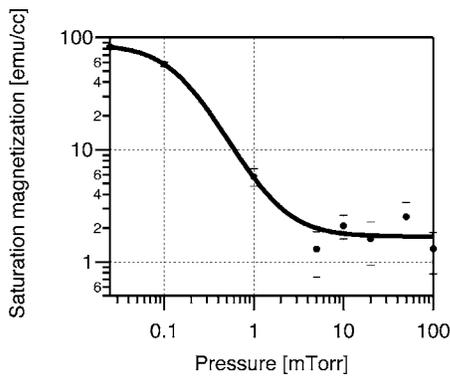
FIG. 3. (Color online) Room temperature saturation magnetization (emu/cc) of Bi–Fe–O films as a function of oxygen pressure during the deposition.

FIG. 4. (Color online) Lattice constant (left) and intensity (right) of (002) $BiFeO_3$ peak observed by microdiffraction as a function of continuously changing film thickness.

creased. Details of the microstructural properties of the $BiFeO_3$–Fe_2O_3 mixture will be reported elsewhere.

Figure 3 shows the saturation magnetization of the various $BiFeO_3$–Fe_2O_3 films ($\approx$300 nm thick) measured by a SQUID magnetometer at room temperature. The magnetization of the bismuth iron oxide films fabricated at oxygen partial pressures higher than 5 mTorr is about 2 emu/cc. This value is consistent with that of pure $BiFeO_3$ thin films previously reported by others.[3,5,7] The magnetization of the films increases steadily as the deposition pressure decreases, and reaches about 80 emu/cc, for the film fabricated at 0.1 mTorr. α-Fe_2O_3 (hematite) is known to exhibit weak ferromagnetism below the Néel temperature ($T_N \approx 950$ K).[8,9] In contrast, γ-Fe_2O_3 is known to display magnetization up to 400 emu/cc at room temperature.[10] Assuming that the magnetization observed here arises from γ-Fe_2O_3, we estimate the volume fraction of γ-Fe_2O_3 to be $\leqslant$20% in the films deposited at less than 1 mTorr. This is consistent with x-ray results shown in Fig. 1, which shows that the γ-Fe_2O_3 peak is only "visible" in the spectra from films deposited at the lowest pressure. This shows that we can controllably tune the magnetization of the Bi–Fe–O films by adjusting the deposition pressure in the 0.1–5 mTorr range, which in turn determines the multiphase mixture ratio.

Our $BiFeO_3$ films have exhibited good piezoelectric properties at room temperature as measured by piezoelectric force microscopy.[11] Magnetostriction in α-Fe_2O_3 as well as γ-Fe_2O_3 has been previously reported.[12,13] The present films, which are epitaxial nanocomposite mixtures of magnetostrictive α-Fe_2O_3 and piezoelectric $BiFeO_3$, thus represent a new type of composite multiferroic material. Investigation of the ME coupling in the $BiFeO_3$–Fe_2O_3 composite films is currently underway.[14]

Stress enhanced magnetization in excess of 100 emu/cc was previously observed in $BiFeO_3$ films.[2] Eerenstein *et al.* have also studied thickness dependent magnetization in $BiFeO_3$ films, but observed no enhancement.[3] To further systematically study the stress enhancement effect in thin films, we grew a $BiFeO_3$ film sample with a continuously changing thickness by a gradient deposition technique using a moving shadow mask.[15] Figure 4 shows the out-of-plane lattice constant and the intensity of the $BiFeO_3$ (002) peak measured by
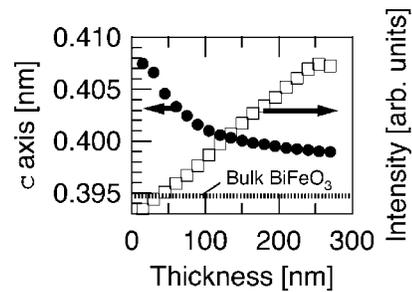
x-ray microdiffraction. The lattice constant decreases, and the peak intensity increases continuously as the thickness increases. This plot indicates that the stress in the film decreases as the thickness increases and the degree of relaxation increases continuously. We have performed scanning SQUID microscopy across this sample and found that the magnetization of the film does not change. X-ray photoelectron spectroscopy of this sample revealed that the valence state of Fe in the film remains 3+ in the thickness range studied here. These results are consistent with those reported by Eerenstein *et al.*[3]

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