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Multiphase growth in Bi-Mn-O thin films

S. Fujino, M. Murakami, S.-H. Lim, L. G. Salamanca-Riba, M. Wuttig, and I. Takeuchi[a]
Department of Materials Science and Engineering, University of Maryland,
College Park, Maryland 20742

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We report on multiphase thin film growth of the Bi-Mn-O system on $SrTiO_3$ (100) substrates. By varying the deposition oxygen partial pressure, the dominant phase formed in the film can be continuously changed from single phase epitaxal multiferroic $BiMnO_3$ to epitaxally grown ferromagnetic Mn_3O_4. X-ray diffraction and transmission electron microscopy revealed that epitaxial multiferroic nanocomposites consisting of $BiMnO_3$ and Mn_3O_4 form when the deposition pressure is ≈ 10 mTorr. The magnetic properties of the films were found to change as a function deposition pressure in a manner consistent with the variation in the nanocomposite microstructure. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2402580]

Multiferroic materials[1,2] and materials showing magnetoelectric (ME) effects[3–5] are of great interest for novel device applications including inexpensive ultrasensitive magnetometers and biferroic memory elements where spontaneous magnetization and charge polarization are coupled. Natural multiferroic compounds such as $HoMnO_3$ (Ref. 2) and $TbMn_2O_5$ (Ref. 3) are rare and typically exhibit ME coupling at low temperatures and under very high magnetic field. Recently, there has been much interest in $BiMnO_3$ as a multiferroic material with a highly distorted perovsikite strucure.[6–9] Moreia dos Santos *et al.* reported on the synthesis of $BiMnO_3$ thin films which displayed the coexistence of ferromagnetic and ferroelectric properties below 105 K.[9–11]

$BiMnO_3$ is generally unstable at 1 atm pressure. Consequently, there is a narrow window of processing conditions to obtain phase pure $BiMnO_3$. In order to fabricate $BiMnO_3$ by the conventional bulk method, high pressure (≈ 6 GPa) and high temperature (≈ 1100 K) processing is required.[12,13] In this study, we report on the multiphase growth and magnetic properties of bismuth manganese oxide thin films deposited by pulsed laser ablation. Coexisting $BiMnO_3$ and Mn_3O_4 phases are observed in the films with a systematically varying degree of mixture controlled by the deposition oxygen partial pressure.

We ablated a stoichiometric $BiMnO_3$ 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 2.5–500 mTorr and 550–750 °C, respectively. The typical deposition rate was 5 nm/min, and $SrTiO_3$ (STO) (001) was used as the substrate. The thickness of all films were 200 nm. Scanning x-ray microdiffraction (using a D8 DISCOVER with GADDS by Bruker-AXS) and transmission electron microscopy (TEM) (using a JEOL 4000-FX) were performed 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. A superconducting quantum interface device (SQUID) magnetometer was used to characterize the magnetic properties of the films.

Figure 1 shows x-ray diffraction (XRD) spectra of the bismuth manganese oxide thin films deposited on $SrTiO_3$ (001) substrates at the deposition temperature of 650 °C under different oxygen pressures from 1 to 20 mTorr. Diffraction was performed using the ω scan mode, and the intensities were integrated in ω between 85° and 95°. Epitaxial $BiMnO_3$ with the (001) orientation were obtained at oxygen partial pressures higher than 5 mTorr, and the intensity of the (002) diffraction peak at $\approx 45.5°$ of $BiMnO_3$ increases as the pressure increases. The peak corresponding to the Mn_3O_4 phase with the (101) reflection at $\approx 36.5°$ is observed when the oxygen pressure is less than 10 mTorr, and the intensity of this peak increases as the oxygen pressure decreases. A mixture of $BiMnO_3$ and Mn_3O_4 phases is observed for deposition pressures between 5 and 10 mTorr. This transition in the dominant phase in the film reflects the change in the amount of the Bi incorporation in the film due to the high volatility of Bi metal. As we decrease the deposition oxygen pressure, the Bi content in the films decreases. At an oxygen pressure of above 20 mTorr, the films are single phase $BiMnO_3$, and we do not observe any impurity phases from XRD. When the deposition temperature is above 750 °C or

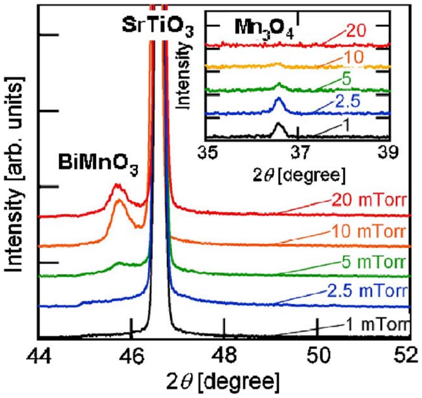

FIG. 1. (Color online) X-ray diffraction spectra (in log scale) of bismuth manganese oxide thin films on the $SrTiO_3$ (001) substrate deposited under different oxygen partial pressures from 1 to 20 mTorr at a deposition temperature of 650 °C.

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[a] Also at Center for Superconductivity Research, University of Maryland, College Park, Maryland 20742; electronic mail: takeuchi@umd.edu

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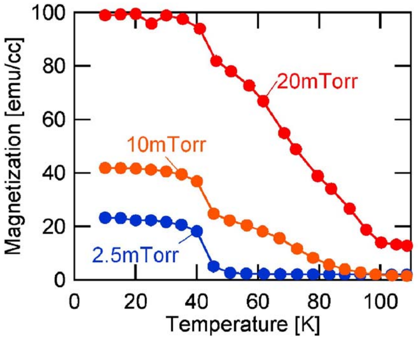


FIG. 2. (Color online) Temperature dependence of magnetization at 1 kOe under an applied magnetic field along the in-plane direction of bismuth manganese oxide thin films on the $SrTiO_3$ (001) substrate deposited under different oxygen partial pressures at a deposition temperature of 650 °C.

below 550 °C and the deposition oxygen pressure is above 50 mTorr, we observe the presence of impurity phases in the films such as Bi_2O_3 and Mn_2O_3.

Figure 2 shows the temperature dependence of magnetization of a series of films grown on $SrTiO_3$ (001) substrates at a deposition temperature of 650 °C at different oxygen pressures. They were measured at 1 kOe applied magnetic field along an in-plane direction. At the low deposition pressure (<5 mTorr), the observed Curie temperature of ≈ 45 K is consistent with that of the Mn_3O_4 phase which is at 42 K. At high pressures, we see the Curie temperature of $BiMnO_3$ which is at about 100–105 K, and we observe an additional increase in magnetization at around 42 K due to the presence of Mn_3O_4. Based on the increase in magnetization, the 20 mTorr film also contains a small amount of Mn_3O_4 phase, even though we could not confirm this by XRD and TEM. In the intermediate range of the deposition pressure (2.5–20 mTorr), we clearly observe the multiphase behavior in magnetization.

Figure 3 shows magnetic hysteresis loops of the Bi-Mn-O films deposited at different pressures at 10 K under an applied magnetic field along the in-plane direction. A continuous change in the curves is observed as the pressure is changed. At low oxygen partial pressure, a high coercive field and a low saturation magnetization are observed, while at high pressures, low coercivity and a high saturation magnetization are observed. This behavior is consistent with the fact that in the high and low pressure limits, the films are almost entirely $BiMnO_3$ and Mn_3O_4, respectively. The values of the coercive field and the saturation magetization are consistent with those of previously reported single phase bulk and films of $BiMnO_3$ (Refs. 6–9) and Mn_3O_4.[14–17] The reported saturation magnetization of $BiMnO_3$ is about $200\ \mathrm{emu/cm^3}$ and that of Mn_3O_4 is about $40\ \mathrm{emu/cm^3}$. In the case of 10 mTorr film, the volume ratio between $BiMnO_3$ and Mn_3O_4 is about 1:1 estimating from the magnetization versus temperature curve. The hysteresis loops of the 2.5 mTorr and 20 mTorr films are more single phaselike, while the film deposited at 10 mTorr displays a multiphase behavior with a deflection at ~ 1 kOe in the curve.

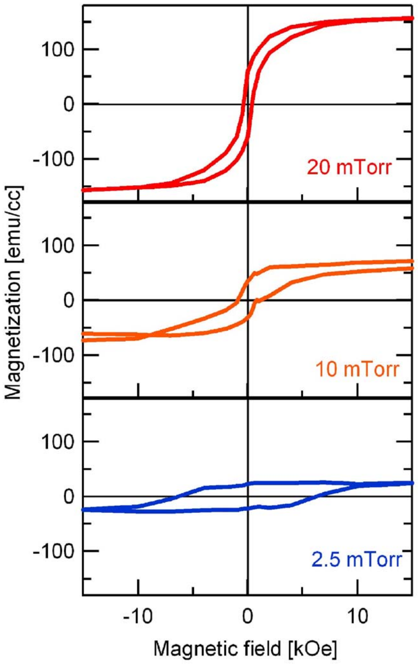
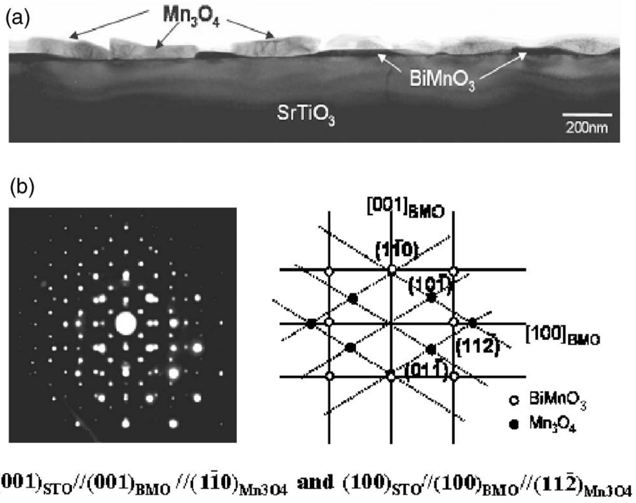


FIG. 3. (Color online) Hysteresis curves at 10 K under an applied magnetic field along the in-plane direction of the Bi-Mn-O films grown on the $SrTiO_3$ (001) substrate at different deposition oxygen pressures at a deposition temperature of 650 °C reflecting the characteristic of $BiMnO_3$ (top), Mn_3O_4 (bottom), and their mixture phases (middle).

Figure 4 shows a cross-sectional TEM image (a) and selected area diffraction pattern (SAD) (b) of the 10 mTorr film. A very thin layer of $BiMnO_3$ has grown in the interfacial region above the substrate. In the upper part of the film, there are Mn_3O_4 grains. This indicates that nucleation of the Mn_3O_4 phase took place at the top of the film after deposition due to the low vapor pressure of Bi. The overall trend is that at lower deposition oxygen partial pressure, there is less Bi incorporation in the films. A careful analysis of series of SAD patterns revealed that Mn_3O_4 is preferentially oriented with [101] normal to the film. However, there are also domains of Mn_3O_4 with other orientations. Figure 4(b) was taken from a region where Mn_3O_4 had grown with the (110)



$$(001)_{STO}//(001)_{BMO}//(1\bar{1}0)_{Mn3O4}\ \text{and}\ (100)_{STO}//(100)_{BMO}//(11\bar{2})_{Mn3O4}$$

FIG. 4. (a) Cross-sectional TEM bright field image and (b) corresponding selected area diffraction pattern of a film deposited at 10 mTorr.

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orientation. Here, the epitaxial relationship among the $SrTiO_3$ substrate, the thin layer of $BiMnO_3$, and Mn_3O_4 is found to be $(001)_{STO}//(001)_{BMO}//(1\bar{1}0)_{Mn_3O_4}$ in the out-of-plane direction and $(100)_{STO}//(100)_{BMO}//(11\bar{2})_{Mn_3O_4}$ in the in-plane direction. We also analyzed a 20 mTorr oxygen pressure film by XRD and TEM but we did not observe any Mn_3O_4 phase. We note that due to the limited sampling area, TEM cannot be used to definitively conclude the absence of the second phase. XRD also often does not have enough sensitivity to detect a trace amount of impurity phases.

We have previously reported that Bi-Fe-O films can form epitaxial composites of $BiFeO_3$ and Fe_2O_3.[18] We have investigated the thickness dependence of the two phase formation behaviors of $BiFeO_3$ and Fe_2O_3.[19] When the thickness of the film is continuously changed from 5 to 300 nm, we observed that Fe_2O_3 starts to form on top of the film for thickness of the film lager than 50 nm at low oxygen pressure (<5 mTorr). This indicates that nucleation of the Fe_2O_3 phase took place on top of the film after the deposition due to the vapor pressure of Bi. The multiphase configuration of 200 nm thick Bi-Mn-O deposited at 0.1 mTorr is similar to that of multiphase Bi-Fe-O. We believe Bi-Mn-O exhibits a similar thickness dependence as Bi-Fe-O.

We have previously synthesized $PbTiO_3$-$CoFe_2O_4$ (Ref. 20) and $BaTiO_3$-$CoFe_2O_4$ nanocomposite multiferroic thin films.[21,22] In particular, the ME coupling was observed in the $PbTiO_3$-$CoFe_2O_4$ nanocomposite using a microwave microscope at room temperature.[23] In these films, eutectic separation of the titanates and ferrites plays a key role in the formation of the nanostructures. In the present Bi-Mn-O film system, the multiphase growth arises from the nonuniform concentration of Bi atoms in the matrix. In principle, there should be elastically mediated magnetoelectric cross coupling between $BiMnO_3$ and Mn_3O_4. Investigation of such a coupling in these films are currently underway.

In summary, we have fabricated a new type of multiferroic nanocomposite film consisting predominantly of $BiMnO_3$ and ferromagnetic Mn_3O_4 whose phase makeup and magnetic properties can be continuously tuned by controlling the deposition oxygen partial pressure.

ACKNOWLEDGMENTS

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