Epitaxial growth and properties of metastable BiMnO₃ thin films

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(Received 22 August 2003; accepted 30 October 2003)

Epitaxial thin films of BiMnO₃ were deposited on single-crystal substrates of (100)-oriented SrTiO₃ by pulsed-laser deposition. Structural analysis by x-ray diffraction, electron diffraction, and transmission electron microscopy (TEM) indicated that the films were monoclinic and twinned with two dominant orientation relationships. The first is (111) BiMnO₃ ∥ (100) SrTiO₃ and ~[101] BiMnO₃ ∥ (010) SrTiO₃; the second is (101) BiMnO₃ ∥ (100) SrTiO₃ and ~[121] BiMnO₃ ∥ (010) SrTiO₃. High-resolution TEM images revealed that there is no reaction or appreciable interdiffusion at the substrate/film interface, despite the high temperature of the substrate during deposition (~1000 K). Magnetic characterization was carried out (both magnetization versus temperature and hysteresis loops) and the results agree with previous reports of a ferromagnetic transition with T_c ~105 K. The actual value of T_c in the films is a few degrees lower than the bulk material, the discrepancy being attributed to strain, nonstoichiometry, or size effects. © 2004 American Institute of Physics. [DOI: 10.1063/1.1636265]

In recent years, there has been growing interest in magneto-electric materials devices. BiMnO₃, a distorted perovskite that crystallizes in the C₃m space group, is known to be ferromagnetic. Its magnetic structure was recently described as resulting from a particular ordering of the occupied d₅ orbitals. The ferromagnetism of this compound, together with the recently experimentally verified ferroelectric behavior, make this material potentially interesting for both technological applications and to study magneto-electric interactions. BiMnO₃ is, however, not a stable phase at 1 atm pressure. The conventional synthesis of bulk BiMnO₃ requires high pressures and high temperatures (on the order of 6 GPa at around 1100 K), and it is therefore a quite inaccessible material for research.

One way to facilitate research on such a material would be its stabilization as a high-quality thin film. Here, we report the use of epitaxial stabilization—the use of interfacial strain energy to favor the desired metastable phase over the equilibrium phase—to grow monoclinic BiMnO₃. Although epitaxial stabilization is often used for the growth of metastable phases, including oxides, this compound presents a substantial challenge for two reasons. First, the volatility of the bismuth at the deposition temperature makes it difficult to achieve high-quality films with a stoichiometric target. Second, the desire for soleley Mn³⁺ in the BiMnO₃ films means that the oxygen partial pressure must be controlled during growth and cooling. In addition, because there is no ambient pressure phase with the same stoichiometry (under ambient pressure the reaction of the metal sesquioxides is 2BiO_3 + Mn_2O_3 → Bi_2Mn_4O_9 + 2Bi_2O_3), special care needs to be taken to ensure a proper homogenization of the target, without compromising the Bi content. Ohshima et al. have used pulsed-laser deposition (PLD) to produce films of Bi₁₋ₓSrₓMnO₃ with 0 ≤ x < 0.3, but their work was focused on the lattice strain and film thickness effect on the magnetic properties, and the film structure and microstructure was not characterized in detail. For example, their structural characterization treated the Bi₁₋ₓSrₓMnO₃ films as pseudocubic materials. In this letter, we report deposition of epitaxial thin films of the monoclinically distorted perovskite BiMnO₃ on a (100) face of the cubic perovskite SrTiO₃ using PLD and structural and magnetic characterization of the resulting thin films. The films have sufficient structural perfection to discern that these BiMnO₃ films on SrTiO₃ are monoclinic and multiply twinned.

The films were deposited using a PLD system equipped with a KrF excimer laser (248 nm, Lambda Physik EMG103MSC) in an on-axis geometry. The substrate was heated using a radiatively heated furnace. The target-to-substrate distance was 6.5 cm. Although growth parameters were varied to optimize the synthesis, the parameters used to grow the sample described here were a substrate temperature of ~968 K, an oxygen pressure of 20 mTorr, a laser fluence of 1.5–2 J/cm², a laser repetition rate of 4 Hz, and a target with a Bi:Mn composition ratio of 1:2:1. The sample was quenched at the completion of growth in 1 atm of oxygen to minimize bismuth desorption from the film during the cooling process.

The PLD target was synthesized as follows. Bi₂O₃ (Aesar, 99.999% purity) and Mn₂O₃ (Aesar, 99.999% purity) with a 1:2:1 molar ratio were ball-milled in isopropanol for
24 h, dried, and subsequently calcined at 973 K for 24 h. The resulting powder was reground and pelleted in a disk shape (Ø=28 mm). This pellet was sintered at 1053 K in a sealed alumina crucible for 8 h.

X-ray diffraction (XRD) patterns were collected using a Picker four-circle x-ray diffractometer with Cu Kα radiation and a graphite monochromator. Cross-section specimens for transmission electron microscopy (TEM) were prepared by a standard method which involves polishing, dimpling, and ion milling at 4–6° at 4 keV. The samples were examined in a JEOL 2010F field emission gun electron microscope operating at 400 kV, providing a point resolution of 0.17 nm. The analytical electron microscopy studies were conducted in a JEOL 4000EX high-resolution electron microscope operating at 400 kV, providing a point resolution of 0.17 nm. The analysis method which involves polishing, dimpling, and ion milling at 4–6° at 4 keV. The samples were examined in a JEOL 2010F field emission gun electron microscope operating at 400 kV, providing a point resolution of 0.17 nm. The analytical electron microscopy studies were conducted in a JEOL 4000EX high-resolution electron microscope operating at 400 kV, providing a point resolution of 0.17 nm.

FIG. 1. θ–2θ XRD scan of a BiMnO3/SrTiO3 film. The full width at half-maximum (FWHM) values for the 404 reflection are 0.44° and 1.1° in 2θ and θ, respectively.

FIG. 2. φ scans of the same BiMnO3 film as in Fig. 1. (a) φ scan made at χ=65.7° of the 110 reflection of the (111)-oriented BiMnO3 in this film. The FWHM value in φ is 2.5°. (b) φ scan made at χ=19.2° of the 110 reflection of the (101)-oriented BiMnO3 in this film. The FWHM value in φ is 1.2°. χ=90° aligns the diffraction vector to be perpendicular to the plane of the substrate. φ=0° is aligned to the [010] in-plane direction of the (100) SrTiO3 substrate.

The low symmetry of the BiMnO3 structure makes the absolute determination of the growth orientation a difficult task. Indeed, the overlap of peaks and significant number of reflections (due to the fact that, although the true structure is monoclinic, the structure can also be described as pseudocubic) precludes making a definitive statement. The φ scans of the 110 reflection for the (111)- and (10–1)-oriented BiMnO3 are shown in Figs. 2(a) and 2(b), respectively. These φ scans offer evidence that both orientations are present based on consideration of the structure factor and peak position. Although supportive of the multioriented film, the BiMnO3 films studied and the low symmetry of BiMnO3, the data are not absolutely conclusive. A complete description of this very complex crystallography will be published elsewhere. The low symmetry nature of the BiMnO3 also necessarily dictates that the nature of the twin geometry is complex. Considering only one of the twins for each orientation, however, the dominant epitaxial relationship can be described as first

(111) BiMnO3 || (100) SrTiO3

with

~[101] BiMnO3 || [010] SrTiO3,

and second

(10–1) BiMnO3 || (100) SrTiO3

with


These orientation relationships were confirmed with electron diffraction (patterns not shown). In pseudocubic notation, the BiMnO3 film is epitaxially aligned pseudocube-on-cube with the cubic perovskite substrate. The specific orientation relationships described above come about because monoclinic BiMnO3 has multiple pseudofourfold symmetric planes that can align with (100) SrTiO3.

Cross-sectional TEM (XTEM) was used to analyze the integrity of the interface. Figure 3(a) shows a low magnification XTEM image of the same BiMnO3 film whose XRD spectra are shown in Figs. 1 and 2. One can see that the interface between the film and substrate is well defined; from these micrographs the film thickness was determined to be approximately 100 nm. The selected-area electron diffraction (SAED) patterns of the film and substrate, taken with the
revealed, as expected, a ferromagnetic transition in a (100) SrTiO$_3$ substrate of the same BiMnO$_3$ film as in Fig. 1. (a) Low magnification image, (b) SAED pattern from BiMnO$_3$ film, (c) SAED pattern from SrTiO$_3$ substrate, and (d) HRTEM image of the film/substrate interface.

incident electron beam along the same direction, are shown in Figs. 3(b) and 3(c). Both are identified as the [010] zone axis diffraction pattern of a pseudocubic perovskite structure. Electron diffraction studies corroborate the pseudocube-on-cube alignment between the film and the substrate. The atomic structure of the film/substrate interface was characterized by high-resolution TEM (HRTEM). Figure 3(d) shows a HRTEM image of the interface with the electron beam along the [010] zone axis of SrTiO$_3$. Both HRTEM and analytical electron microscopy studies indicate that no appreciable interdiffusion occurred despite the high deposition temperature (~968 K).

The magnetic measurements on the same BiMnO$_3$ film revealed, as expected, a ferromagnetic transition (see Fig. 4) with a slight depression of $T_C$ when compared with the bulk value [$T_C$ (Bulk) = 105 K, $T_C$ (Film) = 97 K]. This lowering of the Curie temperature has been observed before in BiMnO$_3$ films and in other systems, and can be attributed to strain, the film being slightly off composition, or the small thickness of the film.

Attempts have been made to measure dielectric properties on these films. Hopping conductivity, however, prevented proper dielectric characterization, possibly due to oxygen nonstoichiometry of the films since Mn can easily take other oxidation states than the nominal 3+.

In conclusion, we have deposited epitaxial thin films of BiMnO$_3$ on SrTiO$_3$. The films show an abrupt interface with the substrate. Magnetic measurements reveal a Curie temperature slightly lower than reported for the bulk material. The depression in Curie temperature can be attributed to a non-stoichiometric composition, strain, or to a size effect.

The work at UCSB was supported by the MRSEC Program of the National Science Foundation (NSF) under Award No. DMR00-80034. The work performed at Penn State and the University of Michigan was supported by NSF through grant DMR-0103354.

![FIG. 3. XTEM images and SAED patterns along the [010] zone axis of the (100) SrTiO$_3$ substrate of the same BiMnO$_3$ film as in Fig. 1. (a) Low magnification image, (b) SAED pattern from BiMnO$_3$ film, (c) SAED pattern from SrTiO$_3$ substrate, and (d) HRTEM image of the film/substrate interface.](image)

![FIG. 4. Magnetization curve of the same BiMnO$_3$ film as Fig. 1 cooled under no applied magnetic field. The inset shows the ferromagnetic hysteresis loop at $T$ = 5 K.](image)