Fabrication of multiferroic epitaxial $BiCrO_3$ thin films

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We report on the growth and multiferroic properties of epitaxial $BiCrO_3$ thin films. Single phase epitaxial thin films were grown on $LaAlO_3$ (001), $SrTiO_3$ (001), and $NdGaO_3$ (110) substrates by pulsed laser deposition. The films display weak ferromagnetism with the Curie temperature of 120 K. Piezoelectric response and tunability of the dielectric constant were detected in the films at room temperature. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2193461]

Despite the recent surge of worldwide interest in multiferroic materials and their magnetoelectric coupling behavior, there have only been a few intrinsic multiferroic materials identified to date.[1–4] Some Bi based oxide systems, namely, $BiFeO_3$ and $BiMnO_3$, are known to display multiferroic properties.[5,6] $BiCrO_3$ is another potentially multiferroic compound. In the 1960s, bulk synthesis of $BiCrO_3$ was reported with a triclinic pseudounit cell with $a=b=0.390$ nm, $c=0.387$ nm, $\alpha=\beta=90.55°$, $\gamma=89.15°$.[7] But due to the difficult high pressure (40 kbar) synthesis, its ferromagnetic and ferroelectric properties have not been unambiguously established.[7,8] We report on the growth of epitaxial single phase $BiCrO_3$ thin films, which show a ferromagnetic Curie temperature at around 120 K and a ferroelectricity at room temperature. The films were fabricated by pulsed laser deposition on $LaAlO_3$ (LAO) (001), $SrTiO_3$ (STO) (001), and $NdGaO_3$ (NGO) (110) substrates.

In order to fabricate $BiCrO_3$ thin films, we ablated a stoichiometric $BiCrO_3$ 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 0.1–50 mTorr and 550–750 °C, respectively. The typical deposition rate was 5 nm/min. Scanning x-ray microdiffraction (using a D8 DISCOVER with GADDS for combinatorial screening by Bruker-AXS) and high-resolution transmission electron microscopy (TEM) were used for the 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 was used to perform magnetic characterization. The ferroelectricity of $BiCrO_3$ thin films at room temperature was probed using piezoelectric force microscopy (PFM) (Ref. 9) and microwave microscopy.[10,11] An epitaxial $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) layer was used as the bottom electrode underneath the $BiCrO_3$ film for the PFM measurement.

Figure 1 shows x-ray diffraction (XRD) spectra of the epitaxial $BiCrO_3$ thin films deposited on LAO (001) and on a LSCO layer (50 nm) on LAO (001). The films were deposited under the optimum condition: the substrate temperature and the oxygen pressure during the deposition were 650 °C and 5 mTorr, respectively. XRD was performed using the ω-scan mode, and the intensities were integrated in χ between 85° and 95°. Epitaxial $BiCrO_3$ films with (001) and (100) orientations (assuming the triclinic structure) were obtained on LAO and on LAO with LSCO, respectively. The inset shows the closeup of the XRD spectra around 47°, which is near the (002) reflection of LAO. The out-of-plane lattice constants of the films are 0.388 and 0.390 nm for the c and a axes, respectively, which are consistent with the previously reported lattice constants of bulk $BiCrO_3$.[7] The two different epitaxial directions may be caused by the lattice mismatch at the film interface. Namely, the in-plane lattice constants of LAO and LSCO are 0.379 and 0.381 nm, respectively. We have also found that $BiCrO_3$ thin films can grow epitaxially with the a axis orientation on STO (001) and NGO (110) substrates (XRD not shown). When the films were not fabricated under the optimum conditions, traces of the Bi_2O_3 phase were detected in the XRD spectra.

Figure 2 shows a cross-sectional TEM image of a 200 nm thick $BiCrO_3$ thin film on a LAO (001) substrate. $BiCrO_3$ has an atomically sharp epitaxial interface with the substrate. No evidence of the second phases was found in these samples by TEM, in agreement with the XRD result in Fig. 1. The inset of Fig. 2 shows the corresponding diffraction pattern of the area. The observed $BiCrO_3$ is triclinic with

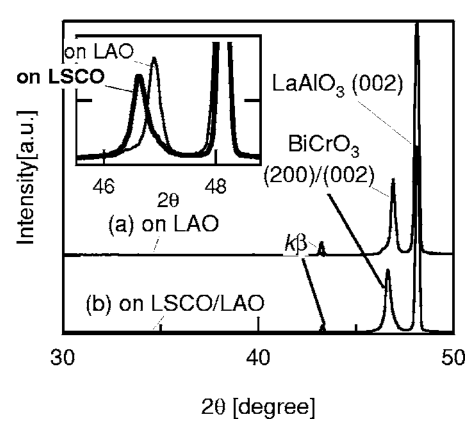

FIG. 1. X-ray diffraction spectra of $BiCrO_3$ thin films fabricated on a (001) $LaAlO_3$ substrate (a) and a $LaAlO_3$ substrate with a $(La_{0.5}Sr_{0.5})CoO_3$ bottom electrode (b). The inset is the close-up of the spectra around the 2θ angle of 47°.

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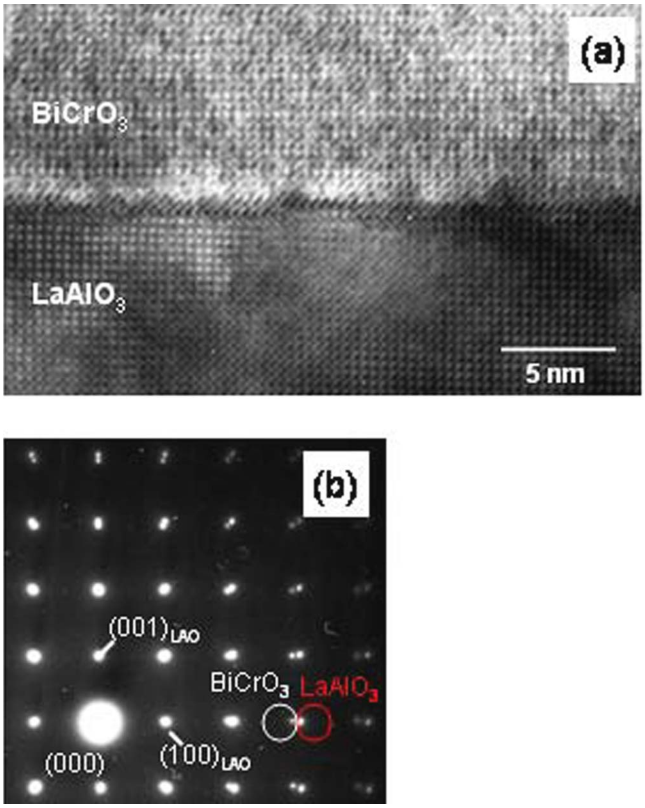

FIG. 2. (Color online) Cross-sectional TEM bright field image (a) and corresponding diffraction pattern (b) of a $BiCrO_3$ thin film fabricated on a $LaAlO_3$ (001) substrate.

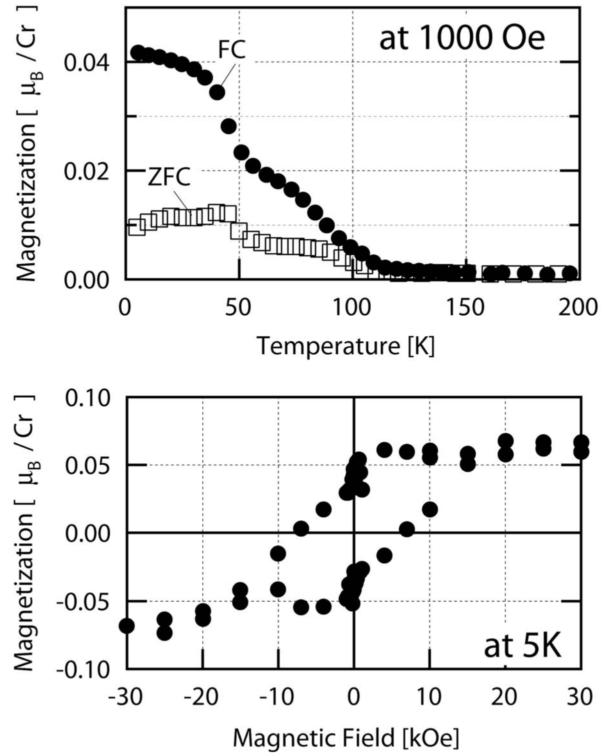

FIG. 3. Temperature dependent magnetization curves (a) and a magnetic hysteresis curve (5 K) (b) of a $BiCrO_3$ thin film fabricated on a $LaAlO_3$ (001) substrate.

lattice constants of $a=b=0.391$ nm, $c=0.388$ nm, $\alpha=\beta=90.6°$, $\gamma=89.1°$, which are in good agreement with the previously reported values.[7] The epitaxial relationship between the substrate and the film was confirmed to be $\langle 001\rangle_{LAO} \| \langle 001\rangle_{BCO}$, and $\langle 001\rangle_{LAO} \| \langle 001\rangle_{LSCO} \| \langle 100\rangle_{BCO}$ (out of plane), and $\langle 100\rangle_{LAO} \| \langle 100\rangle_{BCO}$, $\langle 010\rangle_{BCO}$, and $\langle 100\rangle_{LAO} \| \langle 100\rangle_{LSCO} \| \langle 010\rangle_{BCO}$, $\langle 001\rangle_{BCO}$ (in plane).

Figure 3(a) shows the magnetization versus the temperature curves of a $BiCrO_3$ thin film on a LAO (001) substrate for zero field cooled (open squares) and field cooled (solid circles) measurements with a 1000 Oe magnetic field applied in the in-plane direction. A clear ferromagnetic transition is observed at around 120 K. Figure 3(b) shows a ferromagnetic hysteresis loop of the sample at 5 K. These results are consistent with a previous report by Niitaka *et al.*[8] The magnetic moment of the film is about $0.05\mu_B/\mathrm{Cr}$. The observed magnetic properties are consistent with the picture that the Cr spins are antiferromagnetically coupled and that canting of the spins gives rise to the onset of weak ferromagnetism below 120 K.[7]

Figures 4(a) and 4(b) show, respectively, a topography and an out-of-plane piezoelectric response image of an epitaxial $BiCrO_3$ thin film fabricated on LAO (001) with an LSCO bottom electrode. The images were obtained using the PFM at room temperature. Details of the PFM technique can be found in Ref. 9. Figure 4(a) shows a fairly smooth and homogeneous surface with no indication of impurity phases. The rms roughness of the film was found to be 11 nm. To obtain the piezoelectric response image, the film was first poled at a negative dc bias (−8 V) applied to a conducting

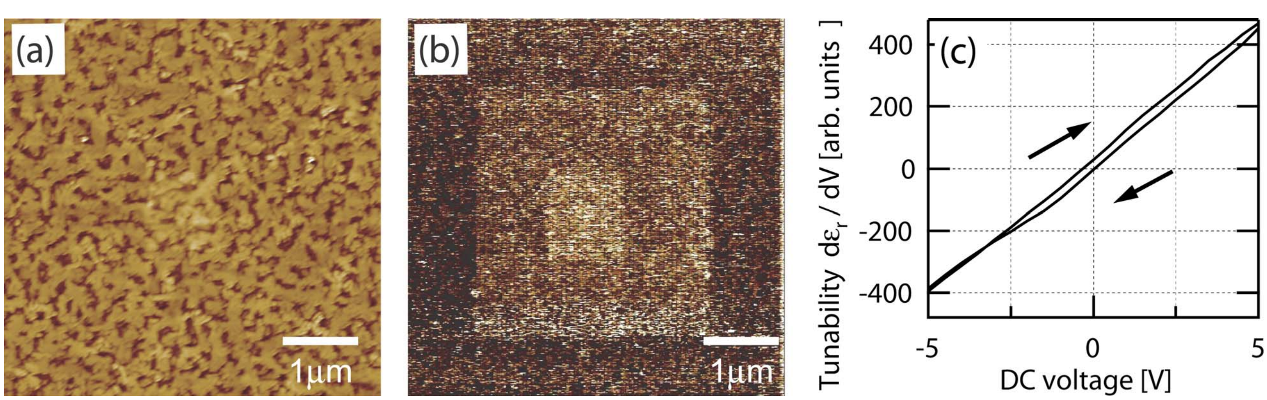

FIG. 4. (Color online) Surface morphology (a) and a piezoelectric force microscopy image (b) (same area) of a $BiCrO_3$ thin film fabricated on a $LaAlO_3$ substrate with a $La_{0.5}Sr_{0.5}CoO_3$ bottom electrode layer. The film in (b) was first poled at a dc bias of −8 V (3×3 μm^2), and then poled at a dc bias of 10 V (1×1 μm^2). A nonlinear dielectric signal measured at 2.4 GHz using microwave microscopy (c). The voltage is measured by the lock-in amplifier. The sample in (c) has no LSCO.

probe while scanning over a $3\times 3\ \mu m^2$ area. Another poling was then performed with a positive voltage (+10 V) during a scan over a $1\times 1\ \mu m^2$ area as shown in Fig. 4(b). The image shows both written regions due to different contrast: the reversible switching indicates the presence of ferroelectricity in the film.

The nonlinear dielectric properties were studied using microwave microscopy as a local probe of the ferroelectricity in film without LSCO.[10,11] The tunability of the dielectric constant is detected using a lock-in amplifier, which monitors the change in the resonant frequency of a microscope cavity (with a resonant frequency of 2.4 GHz), while an ac voltage (5 V, 8 kHz) is applied between the microscope tip and an electrode on the back of the substrate. Figure 4(c) plots the nonlinear dielectric signal as a function of a dc voltage bias applied together with the ac voltage. The nonlinear signal is proportional to $d\varepsilon/dV$, where ε is the dielectric constant and V is the ac voltage. The dc voltage of ±5.5 V is apparently not high enough to observe the expected saturation behavior,[11] but a small hysteresis is observed.

In summary, we have fabricated epitaxial single phase multiferroic $BiCrO_3$ thin films, which display a magnetic Curie temperature of 120 K and show ferroelectricity at room temperature. The magnetoelectric coupling behavior of the films is currently under investigation.

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