Role of oxygen partial pressure and seed layer chemistry in flux mediated epitaxy of single phase multiferroic BiFeO$_3$ thin films

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Multiferroic BiFeO$_3$ (BFO) thin films have been fabricated via flux mediated epitaxy with varying oxygen partial pressure and flux composition (Bi$_2$O$_3$:CuO) conditions. Transmission electron microscopy coupled with energy dispersive x-ray spectroscopy as well as piezoelectric force microscopy confirm, that with the correct flux and seed layer conditions, even at very low partial pressures (3 mTorr) no secondary phases are formed. The study reveals the crucial role of the bottom seed layer and flux chemistry in epitaxy of BFO thin films and provides alternate routes to BFO epitaxy in oxygen-deficient environments. © 2008 American Institute of Physics.

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Bismuth ferrite (BiFeO$_3$ or BFO)-based thin films have recently generated great attention due to promising multiferroic properties. As bismuth (Bi) is a highly volatile element, BFO thin film deposition requires the use of Bi-excess targets or precursors to compensate for the Bi loss at the nominally employed high growth temperatures (>550 °C). As such the optimized growth window for BFO and especially in thin-film form is extremely stringent. Even slightly excess Bi potentially leads to Bi$_2$O$_3$ pockets and since Bi$_2$O$_3$ is a good ionic conductor ($\delta$-Bi$_2$O$_3$, $\sim$1 Ω cm at 800 °C), it can result in high leakage-current density. On the other hand, Bi-deficient films tend to easily form two-phase mixtures comprising of BFO and secondary Fe$_2$O$_3$. It has been argued that such secondary phases question the use of BFO thin films as a model material to investigate multiferroicity.

Recently, we demonstrated that BFO thin films deposited via pulsed laser flux mediated epitaxy (FME) (Ref. 7) show enhanced ferroelectric and dielectric properties without any secondary or parasitic phases thus presenting FME as a solution to the phase-purity challenge. In FME, a flux compound (in this case Bi$_2$O$_3$:CuO) is used to reduce the melting point at the surface and forms a reservoir of Bi required to maintain the film stoichiometry. The vapor ablated from the target material meets the flux on the surface of the substrate, diffuses into the liquid intermediate phase, and finally nucleates on a predeposited seed layer. Since the flux serves as to replenish volatile Bi, low oxygen pressures (and hence cleaner environments) are possible, thereby making this approach tenable for even processes such as molecular beam epitaxy. Of significance is that the liquid phase yields a very large grain size, which can drastically improve dielectric response. Indeed, in our previous work, phase-pure films with much enhanced dielectric properties and superior leakage-current resistance were deposited at oxygen partial pressures as low as 5 mTorr with grain sizes of the order of 1–2 μm. Here we delineate the crucial role of flux and seed layer chemistry during the FME process in obtaining phase-pure BFO thin films by systematically varying oxygen partial pressure and flux composition.

The BFO thin films used in this study were deposited on SrRuO$_3$ (SRO) buffered (001) oriented SrTiO$_3$ (STO) substrates using 10% Bi-excess Bi$_{1.1}$FeO$_3$ targets via pulsed laser ablation (KrF excimer laser λ = 248 nm) ablation. The thicknesses, the growth temperature, and the composition of the flux were kept identical to the previous work, the thicknesses of the BFO thin film (200 nm), flux (40 nm), and seed bottom BFO layer (10 nm) were kept constant in all the samples. Growth temperatures were maintained at 650 °C for the seed layer and flux deposition and 730 °C for the BFO layer. Two different flux compositions (11.7 and 17 vol% of CuO) were used, and the oxygen partial pressure during deposition was 3–30 mTorr. Ferroelectric domain structure was investigated using piezoelectric force microscopy (PFM). Details of the tip and imaging conditions are given elsewhere. Cross-sectional transmission electron microscopy (TEM) (XTEM) and energy dispersive x-ray spectroscopy (EDS) analysis were obtained using the Philips CM200 TEM operated at an accelerating voltage of 200 kV. For the EDS scans, images were captured before and after each scan and only those scans that did not show drift were considered for further analysis.

Figure 1 shows a series of the topographic and PFM images obtained on the FME grown BFO thin films. Figure 1(a) shows the topography of the BFO thin films whose oxygen partial pressure for the entire layers of film (bottom seed layer, flux, and BFO film) has been maintained at 30 mTorr and the CuO content in the flux was at 11.7% (sample 1). Compared to the BFO thin film grown with a conventional pulsed laser deposition on the same SRO/STO system, the sizes of the grains are relatively very large varying from 1 to 5 μm. The simultaneously captured out-of-plane PFM (OP-PFM) image of this as-grown state is shown in Fig. 1(b). Writing experiment, where a dc bias of −10 V was applied to its central 3 × 3 μm$^2$ region, followed by reverse...
bias (+10 V) in a $1 \times 1 \mu m^2$ area, was used to probe the domain switching behavior. The OP-PFM image after applying the dc biases shows distinct domain contrasts [Fig. 1(c)] and hence clearly shows ferroelectric domain switching. For the second BFO thin films, the growth pressure was 30 mTorr and the CuO content in the flux was increased to 17 vol % (sample 2). The surface topography [Fig. 1(d)] of the surface shows a large amount of flux that remains over the film surface. XTEM analysis (will be discussed later) revealed that these deposits grow from within the film and hence can be linked to the initial seed layer. For this film, the OP-PFM before [Fig. 1(e)] and after positive and negative writings [Fig. 1(f)] shows that regions between the flux deposits again have good ferroelectric domain switching. Most importantly, we note that the flux regions remain unaltered to the external electrical perturbation. In the case of third BFO thin films, with lower oxygen partial pressure (3 mTorr) and low CuO (11.7%) in the flux composition (sample 3), the topography is shown in Fig. 1(g). Contrary to the first case and despite using low CuO content, this film also shows a flux region on the surface. The OP-PFM image [Fig. 1(h)] captured simultaneously confirms that these regions constitute the nonferroelectric flux particles which are indicated out by arrows, and similar to Fig. 1(f) the flux region remains inert to the applied electric field [Fig. 1(i)]. Thus the strong role of both oxygen partial pressure as well as flux chemistry is evident in determining the ultimate phase as well as surface properties of the BFO thin film.

Systematic XTEM analyses were carried out on all the three samples to understand interfacial chemistry and its resultant effects on microstructure as well as phase behavior. Figure 2(a) shows the XTEM bright field image of BFO sample 1, with the selected area diffraction pattern (SADP) shown in the inset. This image, along with the SADP, reveals that the BFO thin film is epitaxial with sharp interfaces, and no evidence of an interfacial layer between the seed BFO and the top BFO layer was observed. The SADP confirms the presence of single phase BFO thin films without any secondary phases previously observed for such partial pressures. This is the ideal case of FME and complete structural details can be found in Ref. 7. Figure 2(b) (BFO sample 2 with excess CuO in the flux) shows a highly strained interface between the BFO and the SRO with secondary phase inside the BFO matrix. In agreement with the atomic force microscopy/PFM observation, the surface of this BFO thin film is relatively rough and it shows a significant amount of residual flux. There are distinct threading dislocations across the entire interface (from the strain contrast), and they may be the consequence of the breakdown of the delicate flux-BFO equilibria at the growing surface. Figure 3(a) represents the bright field elastic TEM image and corresponding EDS maps (Cu K [Fig. 3(b)], Bi L [Fig.
hence changes the fraction of Bi$_2$O$_3$ in the liquid flux. This separation mediator, the CuO remains at the matrix without any phase equilibrium, when the flux layer is deposited on this seed BFO layer, the seed layer acts as a reservoir for Bi$_2$O$_3$ and hence raises the melting point; thus there is no driving pressure and temperature. BFO thin film is deposited via this Bi$_2$O$_3$ rich flux, which in turn results in a variation in the flux composition. The binary solid-solubility phase diagram for Bi$_2$O$_3$–CuO shows a relatively deep eutectic point at 90% Bi$_2$O$_3$–CuO. The growth problem is further compounded as fractions outside this eutectic point, the flux surface has a and hence raises the melting point; thus there is no driving pressure and temperature.

For sample 3 BFO thin film, although the XTEM image shows sharp interfaces without any strained region, the optical-diffraction pattern confirming the fcc structure for the Cu flux. Point EDS also confirmed that the flux layer in sample 3 is mainly Cu oxides of Cu have a cubic structure. On the other hand the HRTEM image shows a pattern characteristic of a fcc structure. Using commercial software such as CARINE as well as web-based diffraction analysis we confirmed that none of the possible oxides of Cu have a cubic structure. On the other hand the HRTEM image shows well-defined lattice fringes, and the selective area optical-diffraction pattern of the flux region (inset) shows a pattern characteristic of a fcc structure. Using commercial software such as CARINE as well as web-based diffraction analysis we confirmed that none of the possible oxides of Cu have a cubic structure. On the other hand the HRTEM image shows well-defined lattice fringes, and the selective area optical-diffraction pattern of the flux region (inset) shows a pattern characteristic of a fcc structure. Using commercial software such as CARINE as well as web-based diffraction analysis we confirmed that none of the possible oxides of Cu have a cubic structure. On the other hand the HRTEM image shows well-defined lattice fringes, and the selective area optical-diffraction pattern of the flux region (inset) shows a pattern characteristic of a fcc structure.

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