Ferromagnetism in pseudocubic BaFeO$_3$ epitaxial films

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Growth and properties of epitaxial BaFeO$_3$ thin films in the metastable cubic perovskite phase are examined. BaFeO$_3$ films were grown on (012) LaAlO$_3$ and (001) SrTiO$_3$ single crystal substrates by pulsed-laser deposition. X-ray diffraction shows that films grown between 650 and 850 °C yield an oxygen-deficient BaFeO$_{2.5+x}$ pseudocubic perovskite phase that decreases in lattice spacing with increasing growth temperature. Magnetization measurements on as-deposited BaFeO$_3$ films indicate weakly ferromagnetic behavior. Annealing in 1 atm oxygen ambient converts them into conductive and robustly ferromagnetic pseudocubic BaFeO$_3$ phase with $T_C=235$ K. Observation of ferromagnetism with increasing oxygen content is consistent with superexchange coupling of Fe$^{+4}$−O−Fe$^{+4}$.

Magnetic oxides$^1$ are of interest in understanding magnetic moment interactions, device applications, and coupling via the formation of nanostructured interfaces.$^{2-4}$ BaFeO$_3$ is one of the few oxides where iron assumes an oxidation state of $+4$. In bulk, BaFeO$_3$ normally assumes a hexagonal crystal structure ($a=0.568$ nm and $c=1.386$ nm), although various polymorphs are observed with oxygen deficiency.$^5$ The magnetic properties are dependent on oxygen content, presumably affecting the valence of iron. Bulk hexagonal BaFeO$_3$ exhibits an antiferromagnetic to ferromagnetic transition at 160 K, with a Curie temperature $T_C$ of 250 K.$^6$ More recent Mössbauer and high magnetic field studies contradict this conclusion, showing that no magnetic ordering occurs for 160 K $> T > 220$ K.$^8$ This discrepancy could be related to BaFeO$_{3-x}$ oxygen stoichiometry.$^9$

The properties of BaFeO$_{3-x}$ films can be significantly different from that of bulk material.$^{11-13}$ For epitaxy on (001) SrTiO$_3$, BaFeO$_3$ assumes a metastable pseudocubic crystal structure similar to that observed for SrFeO$_3$. Stabilization of metastable phases via epitaxy has been observed for other perovskitlike oxides.$^{14,15}$ This pseudocubic thin film phase is reportedly ferromagnetic at room temperature,$^{1,12}$ in contrast to the hexagonal bulk phase. This is presumably the result of differences in local atomic bonding that can be affected by lattice structure, strain, and/or defects. Modification through strain has been observed in a variety of perovskite material properties.$^{16-20}$ However, it is unclear how strain might yield an enhancement in $T_C$ for magnetic ordering in the Fe$^{+4}$−O−Fe$^{+4}$ system. The reported lattice constant of the BaFeO$_3$ epitaxial film on SrTiO$_3$ was $a =4.120$ Å, which is larger than that expected based on anion-cation spacing in bulk.$^{21,22}$ The films were also insulating at 300 K. Magnetization measurements showed hysteresis as well as remnant magnetization.$^{11,12}$

In this paper, the properties of epitaxial pseudocubic BaFeO$_{3-x}$ films grown by pulsed laser deposition are examined. As will be seen, the onset of robust ferromagnetism is a strong function of oxygen content, similar to what is seen in the bulk phases.

BaFeO$_3$ thin films were grown on (012) oriented LaAlO$_3$ and (001) SrTiO$_3$ via pulsed laser deposition.$^{21,22}$ LaAlO$_3$ is rhombohedral at room temperature, cubic at the growth temperatures. It can be indexed as a perovskite pseudocubic with $a_0=3.7904$ Å at 300 K. The backside of the substrate was etched with HNO$_3$ in order to remove any trace metals that might introduce spurious magnetic properties. Substrates were prescreened in a superconducting quantum interference device (SQUID) magnetometer to ensure that the substrates were “nonmagnetic” (no ferromagnetic impurities) and, thus, suitable for magnetic characterization of the thin films after growth. Substrates were attached to the heater platen with silver paint. A KrF (248 nm) excimer laser was used as the ablation source. Laser energy densities of 2–3 J/cm$^2$ were utilized. Target to substrate distance was ~4 cm. The ablation targets were BaFeO$_3$ ceramics. The substrate temperatures were between 650–850 °C with an oxygen pressure of 0.1–100 mTorr. The film thickness was 200 nm. After growth, the samples were cooled at 10 °C/min in the oxygen partial pressure used during growth.

The deposited films were examined by x-ray diffraction (XRD) using Cu $K \alpha$ radiation. The x-ray diffraction results show out-of-plane orientation. Magnetic characterization was performed on a SQUID magnetometer. The magnetic field was applied perpendicular to the substrate surface. In some cases, BaFeO$_3$ films were postannealed in oxygen.

Initial studies focused on understanding epitaxy and phase evolution for the $in situ$ grown BaFeO$_{3-x}$ films. Figure 1(a) shows the XRD data for films grown on LaAlO$_3$ in an oxygen pressure of 10 mTorr. In all cases, the growth of BaFeO$_{3-x}$ consistent with a pseudocubic perovskite structure is observed, although not as a single cubic phase. In particular, the diffraction data show the emergence of two distinct peaks which could be two phases or multiple diffraction peaks arising from different orientations of a single phase. At...
low temperatures, the BaFeO$_{3-x}$ (200) peak at 44.27° corresponds to a pseudocubic lattice parameter of 4.09 Å. As the substrate growth temperature is increased, a second peak emerges at 45.13°, corresponding to a lattice spacing of 4.02 Å. This could represent a second cubic phase with a slightly smaller $d$ spacing or a splitting of the peak due to a single, low symmetry phase with different oxygen stoichiometry. Low symmetry phases are seen for SrFeO$_{2.86}$, tetragonal (SrFeO$_{2.97}$), and orthorhombic (SrFeO$_{2.73}$) progression with changes in oxygen stoichiometry. However, additional inplane characterization of the crystal structure suggests that the BaFeO$_{3-x}$ films consist of two pseudocubic phases with slightly different lattice spacing. This result is consistent with that shown in other work on BaFeO$_{3-x}$ films. The as-grown BaFeO$_{3-x}$ thin films grown at 10 mTorr were translucent with an orange-tan color at a film thickness of $\sim$300 nm. The as-grown films were nonconducting. The magnetic properties of the as-deposited BaFeO$_{3-x}$ film were measured at temperatures down to 10 K. The magnetization behavior for the film grown at 750 °C and 10 mTorr is shown in Fig. 1(b). A small but discernable hysteresis is seen in the $M$ versus $H$ plot, indicating that these films are weakly ferromagnetic. Magnetization measurements were made for each of the samples grown at the temperatures, as shown in Fig. 1(a). The SQUID magnetization behavior for each of these as-grown unannealed films was similar to that shown in Fig. 1(b).

To investigate the progression of film properties with oxygen content, several films were subjected to postgrowth annealing in oxygen ambient (1 atm). Films were annealed at 600, 750, or 900 °C for 1 h. This annealing treatment induced a decrease in lattice spacing and resistivity. Figure 2 shows the XRD scans for a BaFeO$_{3-x}$ film on LaAlO$_3$ grown at 700 °C, 100 mTorr O$_2$ before and after a 900 °C anneal in oxygen. Before annealing, the peak at 44.21°, corresponding to a cubic $d$ spacing of 4.10 Å, could be deconvoluted into two closely spaced peaks. After annealing at 900 °C, films were measured to be less resistive. The resistivity was on the order of 100 Ω cm. In addition, the color of the films changed to a reflective brown black. After annealing, the peak shifts to 45.13°, corresponding to a lattice spacing of 4.09 Å. Four-circle XRD was used to characterize the in-plane lattice spacing, determined to be 4.0134 Å. The in-plane XRD rocking curve full width half maximum was $\sim$4°. Note that the shift in $d$ spacing with annealing seen for the film in Fig. 2 was commonly observed for multiple films regardless of whether the films were deposited on LaAlO$_3$ or SrTiO$_3$. The XRD results are shown for the film on LaAlO$_3$ since the separation in substrate and film peak is larger, making the shift in the film peak easy to observe. Similar results were seen for films on SrTiO$_3$. In addition, a reduction in lattice parameter after annealing in oxygen is indicative of increasing oxygen content.

Significant changes in magnetic properties were observed with annealing. SQUID magnetometry measurements for the as-deposited and annealed films were performed at 10, 100, and 300 K. Figure 1(b) shows that the as-deposited samples display weak ferromagnetic behavior. In contrast, annealing the films in oxygen induces a robust ferromagnetic phase with large coercive field. For BaFeO$_{3-x}$ films grown on LaAlO$_3$ and SrTiO$_3$ at 600 °C, then annealed in oxygen at 900 °C, clear hysteresis is observed with a coercive field on the order of 800 Oe. Figure 3(a) shows the magnetization at 5 K as a function of field for films grown on SrTiO$_3$ subjected to various anneals; clearly, the magnetization increases with annealing in oxygen. Figure 3(b) shows the magnetization as a function of temperature for the same films. In this case, $T_C$~235 K. Similar experiments were performed for BaFeO$_{3-x}$ films grown on LaAlO$_3$, although the field cooled/zero field cooled splitting was on the order of 100 K for the film on LaAlO$_3$. The realization of ferromagnetism in fully oxidized BaFeO$_3$ and not in the oxygen-deficient material is consistent with the Kanamori-Goodenough rule for superexchange coupling involving transition metal ions, in which the $d_{e-g}^e$ Fe$^{3+}$–O–Fe$^{3+}$ superexchange interaction should be an...
While these results are inconsistent with earlier reports of another phase with oxygen deficiency. Figure 4 shows plots of remanence ($M_r$), remanence ($M_r$), $T_C$, and the peak in the zero-field cooled data for the BaFeO$_{3-x}$ films grown on SrTiO$_3$. Clearly, the annealing of BaFeO$_{3-x}$ films results in a ferromagnetic phase with a relatively high value of $T_C$. While these results are inconsistent with earlier reports of ferromagnetic behavior at 300 K for insulating BaFeO$_{3-x}$ films, they do show that robust ferromagnetism is observed for fully oxidized pseudocubic BaFeO$_3$ at relatively high temperatures. Given a correlation between conduction, lattice spacing, and ferromagnetism in these films, future work will explore the possibility of developing multiferroic composites involving epitaxial BaFeO$_3$ and thin-film ferroelectric perovskite phases.

In conclusion, as-deposited BaFeO$_{3-x}$ thin films grown on single crystal perovskite substrates were pseudocubic, nonconductive, and weakly ferromagnetic, which differs from that of the bulk BaFeO$_3$. Two phases of BaFeO$_3$ were identified, where formation is dependent on growth temperature and pressure. After annealing in oxygen, the films show ferromagnetism and were conductive. The resistivity was on the order of 100 $\Omega$ cm.

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