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 $Fe^{+4}-O-Fe^{+4}$. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2832768]

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.[5] 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.[5–9] 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.[10] More recent Mössbauer and high magnetic field studies contradict this conclusion, showing that no magnetic ordering occurs for $160\ \text{K} > T > 220$ K.[8] This discrepancy could be related to $BaFeO_{3-x}$ oxygen stoichiometry.[10]

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 perovskitelike oxides.[14,15] This pseudocubic thin film phase is reportedly ferromagnetic at room temperature,[11,12] 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.[12,13] 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 insure 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 $BaFeO_{3-x}$ 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

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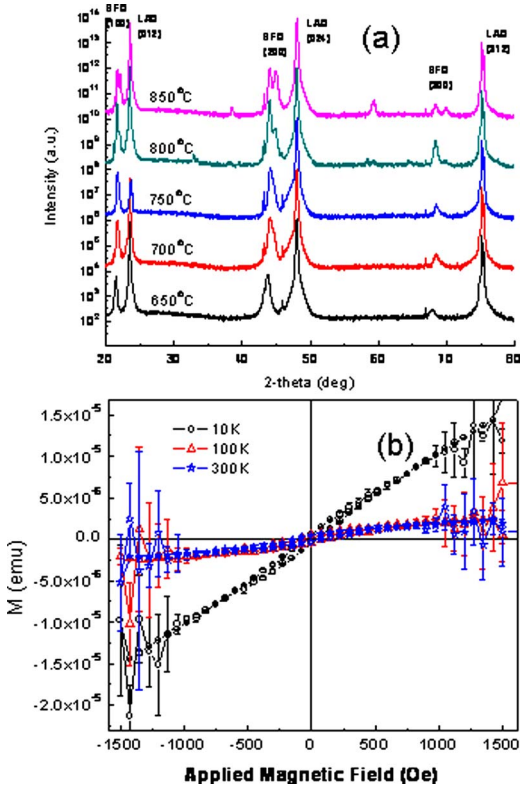

FIG. 1. (Color online) X-ray diffraction scans for $BaFeO_3$ films grown on $LaAlO_3$ (a) at 10 mTorr oxygen pressure at various substrate temperatures. Also shown (b) is magnetization vs applied magnetic field for as-deposited $BaFeO_{3-x}$ grown at 750 °C and 10 mTorr.

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 $SrFeO_x$ ($2.5 \leqslant x \leqslant 3.0$), where there is a cubic ($SrFeO_{2.97}$), tetragonal ($SrFeO_{2.86}$), and orthorhombic ($SrFeO_{2.73}$) progression with changes in oxygen stoichiometry.[23] However, additional in-plane 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.[10,11] The as-grown $BaFeO_{3-x}$ thin films grown at 10 mTorr were translucent with an orange-tan color at a film thickness of ~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 4.009 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 ~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.

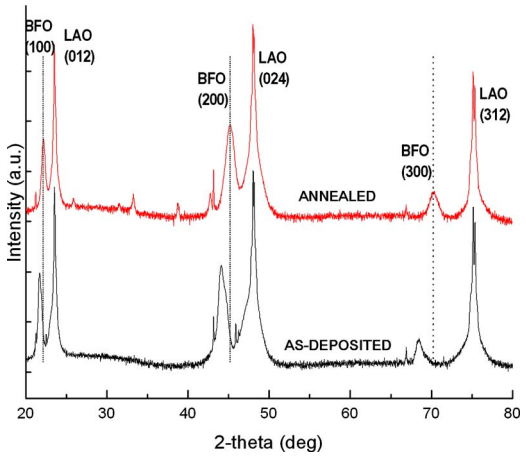

FIG. 2. (Color online) X-ray diffraction scans for $BaFeO_3$ films on $LaAlO_3$, both as deposited and after annealing in 1 atm oxygen for 1 h at 900 °C.

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, $T_C \sim 235$ 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^5-d^5 Fe^{+3}–O–Fe^{+3} superexchange interaction should be an-

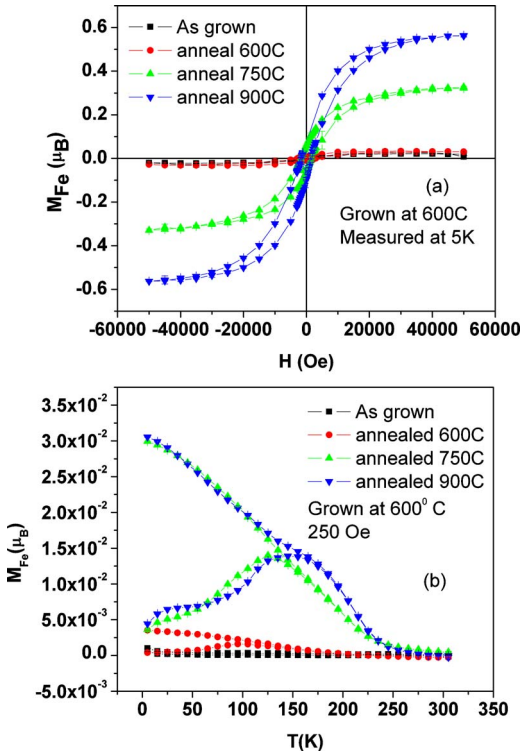

FIG. 3. (Color online) Magnetization vs applied magnetic field for $BaFeO_3$ film grown on $SrTiO_3$ (a) at 600 °C and 100 mTorr plus annealing in 1 atm oxygen for 1 h at various temperatures. The as-grown data is from Fig. 1(b). Also shown is (b) field-cooled and zero field-cooled magnetization as function of temperature for the $BaFeO_3$ film after annealing in 1 atm oxygen for 1 h at varied temperatures. The data are taken in a perpendicular field of 30 kOe.

tiferromagnetic, the d^4-d^4 Fe^{+4}–O–Fe^{+4} superexchange interaction ferromagnetic.[10,24,25] The difference in magnetic behavior for $BaFeO_{3-x}$ films on $LaAlO_3$ or $SrTiO_3$ may reflect a strain effect due to the differing substrate/film lattice spacing and thermal contraction coefficients. Also, the appearance of the bifurcation of magnetic moment for field-cooled/zero field-cooled might be attributed to the competition of antiferromagnetic/ferromagnetic interaction in the film with another phase with oxygen deficiency. Figure 4 shows plots of saturation (M_s), 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

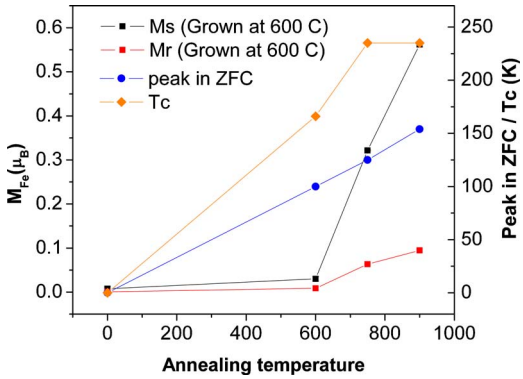

FIG. 4. (Color online) Magnetization results for $BaFeO_3$ films on $SrTiO_3$ showing remanence magnetization, saturation magnetization, zero-field behavior, and T_c as a function of annealing temperature.

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 film, future work will explore the possibility of developing multiferroic composites[2,3] 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 Ω cm.

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[1] *Magnetic Oxide*, edited by D. J. Craik (Wiley, London, 1975).
[2] H. Zheng, J. Wang, S. E. Lofland, Z. Ma, L. Mohaddes–Ardabili, T. Zhao, L. Salamanca–Riba, S. R. Shinde, S. B. Ogale, F. Bai, D. Viehland, Y. Jia, D. G. Schlom, M. Wuttig, A. Roytburd, and R. Ramesh, Science **303**, 661 (2004).
[3] R. Ramesh and N. Spaldin, Nat. Mater. **6**, 21 (2007).
[4] M. Sepliarsky, S. R. Phillpot, M. G. Stachiotti, and R. L. Migoni, J. Appl. Phys. **91**, 3165 (2002).
[5] E. Lucchini, S. Meriani, and D. Minichelli, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **29**, 1219 (1973).
[6] H. J. Van Hook, J. Phys. Chem. **68**, 3786 (1964).
[7] J. Hombo, Y. Matsumato, and T. Kawano, J. Solid State Chem. **84**, 138 (1990).
[8] F. Iga, Y. Nishihara, T. Katayama, K. Murata, and Y. Takeda, J. Magn. Magn. Mater. **104-107**, 1973 (1992).
[9] W. W. Mailnofsky and H. Kedesdy, J. Am. Chem. Soc. **76**, 3090 (1954).
[10] S. Mori, J. Phys. Soc. Jpn. **28**, 44 (1970).
[11] T. Matsui, H. Tanaka, N. Fujimura, T. Ito, H. Mabuchi, and K. Morii, Appl. Phys. Lett. **81**, 2764 (2002).
[12] T. Matsui, E. Taketani, N. Fujimura, T. Ito, and K. Morii, J. Appl. Phys. **93**, 6993 (2003).
[13] E. Taketani, E. Matsui, N. Fujimura, and K. Morii, IEEE Trans. Magn. **40**, 2736 (2004).
[14] D. P. Norton, B. C. Chakoumakos, J. D. Budai, and D. H. Lowndes, Appl. Phys. Lett. **62**, 1679 (1993).
[15] D. P. Norton, J. D. Budai, D. H. Lowndes, and B. C. Chakoumakos, Appl. Phys. Lett. **65**, 2869 (1994).
[16] H.-M. Christen, E. D. Specht, D. P. Norton, M. F. Chisholm, and L. A. Boatner, Appl. Phys. Lett. **72**, 2535 (1998).
[17] H.-M. Christen, L. A. Boatner, J. D. Budai, M. F. Chisholm, L. A. Gea, P. J. Marrero, and D. P. Norton, Appl. Phys. Lett. **68**, 1488 (1996).
[18] D. P. Norton, Mater. Sci. Eng., R. **43**, 139 (2004).
[19] J. Sigman, D. P. Norton, H. M. Christen, P. H. Fleming, and L. A. Boatner, Phys. Rev. Lett. **88**, 097601 (2002).
[20] K. H. Kim, D. P. Norton, J. D. Budai, M. F. Chisholm, B. C. Sales, D. K. Christen, and C. Cantoni, Phys. Status Solidi A **200**, 346 (2003).
[21] D. H. Lowndes, D. B. Geohegan, A. A. Puretzky, D. P. Norton, and C. M. Rouleau, Science **273**, 898 (1996).
[22] D. P. Norton, in *Pulsed Laser Deposition of Thin Films*, edited by R. Eason (Wiley, Hoboken, NJ, 2007), pp. 3–31.
[23] M. Takano, T. Okita, N. Nakayama, Y. Bando, Y. Takeda, O. Yamamoto, and J. B. Goodenough, J. Solid State Chem. **73**, 140 (1988).
[24] J. Kanamori, J. Phys. Chem. Solids **10**, 87 (1959).
[25] J. B. Goodenough, Phys. Rev. **100**, 564 (1955).