APPLIED PHYSICS LETTERS VOLUME 78, NUMBER 17 23 APRIL 2001

Ferroelectricity and ferrimagnetism in iron-doped $BaTiO_3$

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(Received 25 October 2000; accepted for publication 22 February 2001)

The structural and physical properties of pseudocubic thin-film $BaTi_{1-x}Fe_xO_3(0.5\leq x\leq 0.75)$ grown by pulsed-laser deposition are reported. This material is of interest because the corresponding bulk compounds have hexagonal structure for comparable x, and because the films are both ferroelectric and ferrimagnetic well above room temperature. A substantial increase of the ferroelectric transition temperature relative to that of bulk $BaTiO_3$ is attributed to lattice expansion induced by Fe doping. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1367311]

Crystalline compounds in which magnetic and electric polarization coexist are quite rare in nature,[1] particularly at room temperature and above. They offer the prospect of devices in which, e.g., the magneto- or electrostriction may be used to manipulate the polarization or transition temperature. Progress has been made in growing such materials in thin-film form using pulsed-laser deposition (PLD).[2] Recently we reported structural characterization of PLD-grown thin-film $BaTi_{1-x}Fe_xO_3(0.5\leq x\leq 0.75)$ having the pseudocubic perovskite structure.[3] The high Fe concentration of the films implies an extension of the stability limit found for bulk pseudocubic $BaTiO_3$(BTO); Fe doping in the bulk stabilizes the hexagonal perovskite structure[4] for $0.06\leq x\leq 0.84$.[5] Here we present measurements of physical properties for these films, establishing the coexistence of magnetic and electric order well above room temperature.

Thin films were grown by pulsed-laser deposition using a 248 nm KrF excimer laser (Lambda Physik, Compex 205) from polycrystalline targets of $BaTi_{0.5}Fe_{0.5}O_3$, $BaTi_{0.25}Fe_{0.75}O_3$, and $Ba_4Fe_4Ti_3O_{16}$(BFTO-E), prepared by solid state reaction.[3,5] The energy density at the target was $\sim$1.3–2.0 J/cm^2, pulse repetition rate 10–20 Hz, and target-substrate distance 4 cm. The films were deposited on MgO substrates of [100], [110], and [111] orientation, and [100] $SrTiO_3$, with substrate temperature 880 °C and oxygen pressure, $P_{O_2}=100$ mTorr. After deposition, films were held at 500 °C and $P_{O_2}=500$ Torr for 30 min, then cooled to room temperature. Film thicknesses ranged from $\sim$30–360 nm. Measurements of x-ray diffraction (XRD) (Philips X'Pert), electrical resistivity (Keithley 6512 electrometer and Keithley 230 voltage source), and magnetization [Quantum Design superconducting quantum interference device magnetometer, field parallel to the film plane] were performed. Films deposited on 0.05 wt% Nb-doped $SrTiO_3$(STO:Nb) substrates with thermally evaporated Au or Cr–Au overlayers were employed for capacitance measurements (HP4263B *LCR* meter).

Electron microprobe analysis indicated film compositions consistent with those of the targets. Studies of the microstructure of the film by transmission electron microscopy (TEM) and XRD are presented in detail elsewhere,[3] and are summarized here. The pseudocubic perovskite phase with high Fe content forms during initial stages of growth; its metastability is reflected in the competing growth of a disordered phase, composed of hexagonal and pseudocubic intergrowths, during the latter stages of deposition. The crossover thickness is greatest for [100] substrate orientations. We restrict our discussion in the present work to films grown on [100] substrates with thicknesses well below the crossover value of $\sim$1 μm.

TEM and XRD pole figures confirmed cube-on-cube, epitaxial growth of the pseudocubic phase with out-of-plane lattice parameter $a_\perp\simeq 4.03\,\text{Å}-4.07\,\text{Å}$. The actual structure of the as-prepared films is weakly tetragonal or orthorhombic as confirmed by asymmetric rocking curve scans[6] of the {303} film reflections; the average in-plane lattice parameter $\overline{a_\parallel}$ of the as-prepared films is $\sim$0.3% larger than $a_\perp$ at room temperature. Rocking curve scans of the (00ℓ) reflections yield full width at half maximum $\sim$0.6–0.9°, consistent with TEM observations of low-angle grain boundaries. An expanded lattice compared to bulk BTO (bulk tetragonal BTO has[7] $a=3.9947\,\text{Å}$, $c=4.0336\,\text{Å}$ at room temperature) is observed for films grown on both MgO and STO, i.e., is independent of lattice mismatch (opposite in sign for the two substrates: $a^{\text{MgO}}=4.213\,\text{Å}$, $a^{\text{STO}}=3.905\,\text{Å}$).

There are several possible causes for the lattice expansion. Substitution of Fe in BTO implies[8] the oxidation of Fe^{3+} to Fe^{4+} and/or the formation of one oxygen vacancy for two Fe^{3+}. Oxygen vacancies in perovskites expand the lattice.[9] Fe^{3+} substitution for Ti^{4+} also implies a lattice expansion due to the larger radius of the former ion.[10] The unit-cell volume of the films increases with Fe doping at a rate of approximately $2.8\times 10^{-2}\,\text{Å}^3/\%\text{Fe}$ for the fixed P_{O_2} used during growth. This suggests that lattice expansion due

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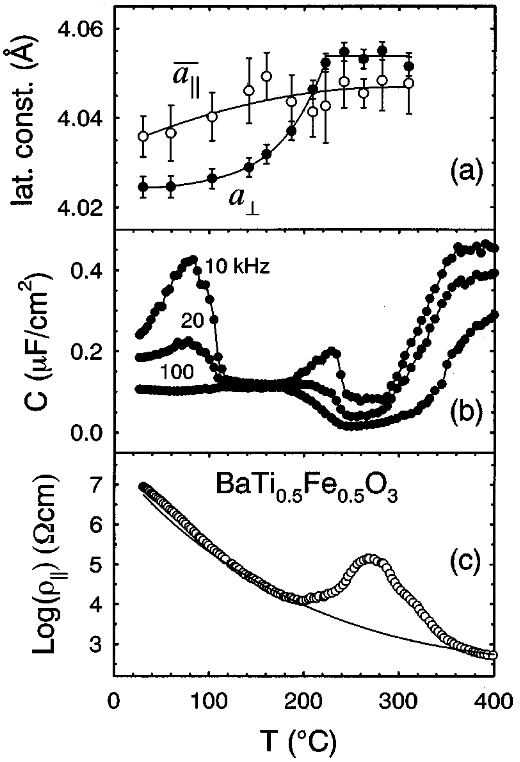

FIG. 1. (a) Average in-plane ($\overline{a}_{\parallel}$) and out-of-plane ($a_{\perp}$) lattice parameters vs temperature during heating in air for a $BaTi_{0.5}Fe_{0.5}O_3$ film grown on [100]STO, (b) capacitance for a Cr–Au/$BaTi_{0.5}Fe_{0.5}O_3$/[100]STO:Nb capacitor, (c) in-plane electrical resistivity for a film of the same composition grown on [100]MgO.

to mechanisms sensitive to P_{O_2} (e.g., thermal vibration and ion peening)[11] play a lesser role.

The temperature evolution (heating in air) of $a_{\perp}$ and $\overline{a}_{\parallel}$ for a $BaTi_{0.5}Fe_{0.5}O_3$ film grown on STO are shown in Fig. 1(a). The structure remains weakly tetragonal (or orthorhombic) at all temperatures. The $\overline{a}_{\parallel}$ increases smoothly with increasing T. The $a_{\perp}$ increases sharply above $T \sim 180\,°C$ and becomes T independent for $T \geqslant 230\,°C$.

The temperature-dependent capacitance for a film of the same composition is shown in Fig. 1(b). Two step-like anomalies are evident upon heating in air at ~100 and ~230 °C, respectively. These are reminiscent of those observed at the orthorhombic-tetragonal (o-t) and tetragonal-cubic (Curie) transitions in the a-axis dielectric constant of bulk BTO, though the transition temperatures are both ~100 °C higher than in BTO. The absence of hysteresis in polarization-field measurements[12] and $\overline{a}_{\parallel}/a_{\perp} < 1$ is consistent with an in-plane orientation of the polarization. Similar $C(T)$ data were obtained for films grown from the other targets, but with differing transition temperatures (see below). The diffuse and dispersive character of the transitions is typical of thin-film ferroelectrics, attributable to disorder and strain inhomogeneity.[13] The broad, dispersive maximum in $C(T)$ evident for $T > 300\,°C$ is a characteristic of bulk perovskites[14] attributed to space-charge relaxation. The room-temperature dielectric constant inferred from the data at 100 kHz is ~40.

The assignment of the higher-T transition to the Curie temperature is supported by the observation of a positive-temperature-coefficient of resistance (PTCR) anomaly[15] in the in-plane resistivity at the same temperature for a $BaTi_{0.5}Fe_{0.5}O_3$ film grown on MgO [Fig. 1(c)]. This phenomenon, typical of polycrystalline BTO, is associated with a potential barrier at grain-boundary Schottky contacts that is controlled by the high-field dielectric constant (ϵ) of the semiconducting grains; the barrier height (and resistivity) increase as T increases above T_C due to a sharp decrease in ϵ.

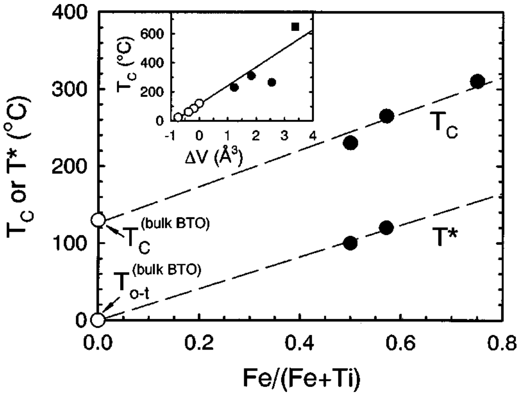

FIG. 2. Transition temperatures vs Fe concentration for films (filled circles) and pure BTO (empty circles), inset: T_C vs volume difference from that of bulk BTO at ambient pressure; empty circles refer to bulk BTO under various pressures (Ref. 18), filled circles to films from the present work, and filled square to a BTO film (Li *et al.*, Ref. 19). The solid line is a linear fit to the bulk BTO data.

It is expected that the background resistivity (the portion not influenced by PTCR) is determined by the concentrations of Fe^{3+} acceptors and oxygen-vacancy donors. Taking 0.42 and 0.1 eV for the corresponding ionization energies, respectively,[16] band parameters appropriate for BTO and electron and hole mobilities[16] of 0.3 cm²/V s, yield a calculated[17] $\rho(T)$ that reproduces the background [solid curve, Fig. 1(c)] with $N_a = 3.8 \times 10^{17}\,cm^{-3}$ and $N_d = 3.05 \times 10^{17}\,cm^{-3}$. Similar calculations for other films and compositions yielded N_a in the range 10^{17}–$10^{22}\,cm^{-3}$ and p-type conduction.

Upon cooling, the anomalies in both $\rho(T)$ and $C(T)$ are absent and also the lattice parameters exhibit thermal hysteresis. Further investigations are underway to determine whether the films remain ferroelectric after heat treatment.[12]

The Fe doping dependencies of the two transitions, designated T^* and T_C, respectively, are shown in Fig. 2. Both characteristic temperatures extrapolate approximately linearly to the values of $T_{o\text{-}t}$ and T_C, respectively, for bulk BTO. Given that applied hydrostatic pressure[18] reduces T_C in bulk BTO, it is plausible that lattice expansion is the source of T_C enhancement for the present films and for undoped BTO films reported previously.[19] In support of this hypothesis is the inset of Fig. 2 where we plot T_C vs ΔV, the volume difference from that of bulk BTO at ambient pressure [ΔV for bulk BTO was computed from the bulk modulus[20] (1.7 Mbar) and the applied pressure from Ref. 18]. The bulk data extrapolate close to $T_C(\Delta V)$ for the Fe-doped (solid circles) and undoped (solid square) films.

Magnetization vs field and temperature, corrected for the substrate contribution, are shown in Fig. 3 for a film grown from the BFTO-E target on [100]STO. Extrapolation of $M(T)$ to beyond the measurement range ($T \leqslant 350\,K$) suggests that the magnetic Curie temperature of this material

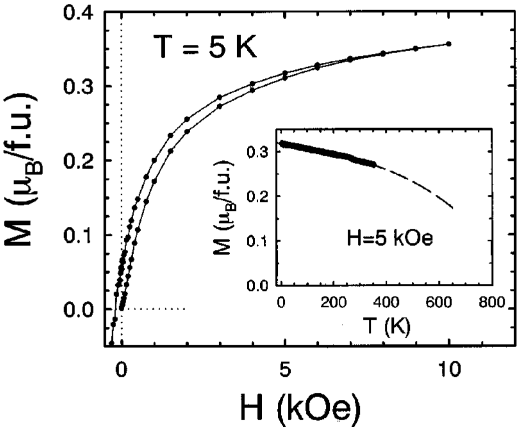

FIG. 3. $T=5$ K magnetization vs applied field for a film grown from BFTO-E on [100]STO. The inset shows $M(T,5\text{ kOe})$ for the same film. The dashed line is a guide.

exceeds 500 °C. The coercive field at $T=5$ K is $H_C = 150-200$ Oe. The $T=5$ K saturation magnetization averaged for several specimens grown from the three targets is $0.35\pm0.05\mu_B$/f.u. This rather small value implies ferrimagnetism. We have performed preliminary calculations[12] that assume a random arrangement of Fe^{3+} and Fe^{4+} moments (spin 5/2 and 2, respectively; Landé g factor taken as 2), and nonmagnetic Ti^{4+} ions on a cubic lattice, Fe/Ti ratio given by the nominal stoichiometry, and antiparallel nearest-neighbor spins. For Fe^{3+} concentrations varying within the broad range implied by the resistivity estimate above, the calculated and measured moments agree to better than a factor of 2.

We have reported on the physical properties of epitaxial, pseudocubic thin-film $BaTi_{1-x}Fe_xO_3$ with high Fe concentration. The material is both ferrimagnetic and ferroelectric well above room temperature. The enhancement of the ferroelectric T_C above that of bulk BTO is associated with a lattice expansion attributed to the combined influence of oxygen vacancies and ionic size effects. Studies to determine the Fe valency and to address the sensitivity of the films to heat treatment are underway.

The work at the University of Miami was supported, in part, by NSF Grant Nos. DMR-9504213 and DMR-9631236. The use of brand names or trade names does not imply endorsement of the product by NIST.

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