LaMnO₃ effects on the ferroelectric and magnetic properties of chemical solution deposited BiFeO₃ thin films

S. Habouti, C-H. Solterbeck, and M. Es-Souni

Institute for Materials and Surface Technology (IMST), Kiel University of Applied Sciences, Grenzstrasse 3, D-24149 Kiel, Germany

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Thin films of the BiFeO₃–LaMnO₃ solid solution were processed on (111)-Pt/Ti/SiO₂/Si substrates via spin coating. Microstructure, and leakage current, ferroelectric and magnetic properties are reported. It is shown that the addition of 5 mol % LaMnO₃ substantially improves the properties. Leakage currents that are several orders of magnitude lower than those of pure BiFeO₃ were obtained. The leakage currents follow the Poole-Frenkel mechanism, and a trap depth of 0.94 eV was obtained. The addition of LaMnO₃ resulted in saturated polarization hysteresis loops with a high remnant polarization \(2P_r \) of 88 \(\mu\)C/cm\(^2\). Finally, LaMnO₃ also leads to higher coercive fields but smaller saturation magnetization. © 2007 American Institute of Physics. DOI: 10.1063/1.2786057

I. INTRODUCTION

BiFeO₃ (BFO) is a model multiferroic material which has received, and still receives, great interest. Its distorted rhombohedral structure belongs to the polar \(R3c\) space group. The high relative ionic displacements along the [111] polar direction and the high Curie transition temperature of 810 °C would impart to this material high polarization properties. Moreover BFO is antiferromagnetic with canted spins, and shows weak ferromagnetism due to its polar \(R3c\) structure. Its Néel temperature of 380 °C would imply multiferroism at room temperature, and this is unique among monolithic materials.

However, one of the well known crucial concerns about BFO is its low resistivity which would prevent polarization switching. The leakage current may be reduced by adapting two different strategies: (i) via improving microstructure and, in particular, reducing the grain size, and (ii) via appropriate doping. In pure BFO, the leakage current mechanism seems to be governed by deep ionized traps purportedly due to the existence of \(\text{Fe}^{2+}\) species. Stabilizing the \(\text{Fe}^{3+}\) ions would therefore help improve the resistivity of BFO.

The present paper aims at investigating the effects of LaMnO₃ additions on the properties of BFO thin films. Although the LaMnO₃ (LMO)–BiFeO₃ system has been investigated in the case of ceramics, a detailed investigation of the microstructure and properties of such a system, particularly as thin film, is still lacking. In this work we have chosen the chemical solution deposition method as well as a versatile (111)-Pt/Ti/SiO₂/Si substrate for film deposition.

II. EXPERIMENTAL

The starting reagents for the precursor solution preparation are Bi-acetate (ABCR, Germany), La-acetate (Fluka, Germany), and Mn- and Fe-acetylacetonate (Alfa Aesar, Germany). Appropriate amounts of the reagents were dissolved in the above order in an aqueous solution containing 1 part of acetic acid for 2 parts of distilled water and finally diluted to a concentration of 0.23 mol/l. The precursor solutions were prepared to yield LMO-BFO film stoichiometries with 0 mol % (BFO), 5 mol % (BFO-LMO), and 10 mol % (BFO-10LMO). The thin films were fabricated via spin coating on a commercial (111)-Pt/Ti/SiO₂/Si substrate heterostructure. Six coating sequences were performed, corresponding to an ellipsometric thickness of 235 nm. Pyrolysis was conducted on the hot plate at 260 °C. Final annealing was performed in a preheated tube furnace in a saturated oxygen atmosphere at 600 °C for pure BFO and 650 °C for BFO-LMO. The annealing time was 60 min. The microstructures were checked using x-ray diffraction (XRD) and atomic force microscopy (AFM) (SIS GmbH, Herzogenrath, Germany). For electrical measurements, round platinum electrodes of 0.6 mm diameter were sputtered to provide the front contact and subsequently annealed for 15 min at 400 °C.

The polarization hysteresis properties were investigated at room temperature by means of a sawyer tower. Voltage- and temperature-dependent leakage currents were measured using a computer controlled stepup including a high-precision electrometer (Keithley 6517A) and a heating stage which allows the temperature to be controlled with an accuracy of ±0.2 K. Current density–voltage (J-V) characteristics were acquired in the step mode with a delay time from 30 to 200 s to allow for sample discharging. The signal was applied to the bottom electrode in all cases. The temperature was measured with a thermocouple placed on the sample surface. The magnetic properties were obtained at room temperature using a vibrating sample magnetometer (ADE Magnetics, Westwood, MA).

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the film stoichiometries investigated. As far as the resolution of the XRD sys-
tem used allows, a pure perovskite phase can be asserted for all compositions. The pronounced 100 fiber texture seen for the pure BFO and BFO-5LMO films is characteristic for sol-gel processed films, and has been attributed to crystallization from the amorphous phase being controlled by low interfacial energies, and not by crystallographic orientations with the substrate. Addition of higher LMO amounts, e.g., 10 mol %, leads to a substantial decrease in the intensity of the 100 reflection, accentuating the polycrystalline microstructure of the film.

The grain morphology as a function of the LMO content is illustrated in the AFM images (Fig. 2). Nondoped BFO has been presented elsewhere, and was shown to be characterized by large grains, approximately 500 nm in size. Although the annealing temperature of BFO-LMO is higher, the mean grain size is decreased which might be attributed to solute effects on grain growth known for many systems in standard textbooks. A close look at the phase image of BFO-5LMO reveals no additional features other than topographical ones, and suggests that the films are free from parasitic phases. Further increase in the LMO content, e.g., BFO-10LMO, leads to increasing the grain size from 70 nm (root mean square) for BFO-5LMO to 100 nm for BFO-10LMO. Furthermore the AFM phase image indicates the presence at grain boundaries of small features, approximately 50 nm in size, whose darker contrast suggests second phase particles. A longer annealing time of 90 min at 650 °C did lead to the appearance of a second phase. These results suggest that the continuous solid-state solubility reported for the system LaMnO₃–BiFeO₃ should be revisited, at least for thin films.

According to the common opinion, the reason for the high conductivity of BiFeO₃ materials is the existence of Fe²⁺ ions which can be oxidized to Fe³⁺ giving rise to one electron in the conduction band. This high conductivity is the most acclaimed hindrance for ferroelectric polarization switching in this material. Furthermore the existence of Fe²⁺ species has been controversially discussed in the literature as being responsible for the high saturation magnetization reported in some papers. The films were therefore analyzed using x-ray photoelectron spectroscopy (XPS). The results are displayed in Fig. 3 for Fe 2p. The binding energies of Fe³⁺ have been reported to be 711.1 eV for the Fe 2p₁/₂ line and 724.7 eV for Fe 2p₃/₂, whereas the same lines have been shown to be located at 709.5 and 719 eV for Fe²⁺. In the present case we observe, after Gaussian peak fitting, peak energies at 710.5 and 724.1 eV for Fe 2p₁/₂ and Fe 2p₃/₂, respectively. Both peaks have a negative shift of about 0.6 eV with respect to those reported above, but are far from the peak energies corresponding to the Fe²⁺ oxidation state. The peak at 718.2 eV is the satellite of Fe³⁺ 2p. Therefore it may be inferred that Fe is present in the oxidation state Fe³⁺ in our films.

The leakage current curves at room temperature are
illustrated in Fig. 4(a) for the stoichiometries investigated. The beneficial effect of LMO doping at low concentration is evident. However, as LMO increases beyond 5% the property deteriorates.

The leakage current mechanism was further studied for the 5% composition since its high resistivity allowed experiments at different temperatures to be performed for extracting the activation energy of the process. The most plausible mechanism to be considered is probably Poole-Frenkel (PF), since the leakage current curves are fairly symmetrical with respect to zero dc voltage. The PF mechanism of conduction is generally described13 by

\[ J \propto E \exp \left[ -\frac{q(\phi_B - \sqrt{qE/\pi\varepsilon})}{k_B T} \right], \tag{1} \]

where \( E \) is the electrical field, \( q \) the elemental charge, \( T \) the absolute temperature, \( \phi_B \) the trap height, \( \varepsilon \) the optical frequency dielectric constant, and \( k_B \) the Boltzmann constant. According to Eq. (1), \( \log(J/E) \) should be linear versus \( E^{1/2} \) which is true in a wide range of voltages, as displayed in Fig. 4(b). Effective activation energies of conductivity, \( E_{\alpha} \), at various applied bias fields were found from linear fits of \( \log(J/E) \) versus \( T^{-1} \) (not shown). Figure 4(c) illustrates the linear regression fit of \( E_{\alpha} \) vs \( E^{1/2} \) which on extrapolation leads to a trap depth of 0.94 eV. This trap depth is quite similar to what is generally found for lead-zirconate-titanate (PZT) thin films,14 and is generally ascribed to ionized oxygen vacancies. A slightly lower trap depth of 0.65 to 0.8 eV has been recently reported for epitaxial BFO films processed vial pulsed laser ablation15 whereby conduction has been attributed to Fe\(^{2+}\) species. It is thought that trap depths associated with Fe\(^{2+}\) should have higher energies, since from thermodynamical considerations the energy necessary for ionization of Fe\(^{2+}\)\(\rightarrow\)Fe\(^{3+}\)+1e lies in the range of 3 eV. In previous work,7 we have, in fact, obtained a trap depth of 2.6 eV for pure BFO. Doping thus changes the nature of traps, and the presence of Fe\(^{2+}\) no more dominates conduction in this material. However, beyond 5 mol % LMO the leakage current properties deteriorate for reasons which cannot be investigated yet.

The ferroelectric hysteresis curves are shown in Fig. 5. Pure BFO shows no switching polarization and had the character of a leaky dielectric. The 10% composition did show ferroelectric polarization but the hysteresis curve is characterized by high conductivity. Correction by subtracting the leakage current failed because the capacitors broke down during measurements. Thus true polarization of the 10% composition remains unknown. In the case of the 5% composition a well-shaped, almost square hysteresis loop was obtained, and was reproducible for all capacitors measured. The remnant polarization, \( P_r \), obtained at room temperature was approximately 45 \( \mu \)C/cm\(^2\). The coercive field, \( E_c \), of 215 kV/cm lies well in the range where the leakage current density is small (approximately \( 2 \times 10^{-6} \) A/cm\(^2\)). Both values are smaller than those reported for pulsed laser deposition (PLD) processed heteroepitaxial films.15 However, since we are dealing with polycrystalline films, where polarization should be a fraction of that along the [111] direction, the results seem to be plausible.

Finally, the magnetic properties are illustrated in Fig. 6 where the magnetization hysteresis curves of the different stoichiometries investigated are compared. The highest saturation magnetization is obtained for the pure BFO film which might be due to the presence of parasitic phases.10 The saturation magnetization decreases for LMO doped in comparison to pure BFO but increases with increasing LMO concentration. Also the coercive field increases with LMO content. The higher coercive fields obtained in this work are in line with the results recently reported for Mn-doped BFO,16 but
the high saturation magnetization values obtained in the same work cannot be confirmed here. The improvement of the magnetic properties of Mn-doped BFO has been discussed in terms of the effects of Mn on suppressing the spiral antiferromagnetic \( G \)-type structure of BFO.\(^{16}\)

**IV. CONCLUSIONS**

In conclusion the beneficial effects of LaMnO\(_3\) addition on the ferroelectric, leakage current, and magnetic properties of BFO have been shown. Promising ferroelectric and magnetic properties may be inferred and encourage further studying this system, concentrating on microstructural changes and their effects on the properties.

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