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Citation: [Applied Physics Letters](#) **90**, 052906 (2007); doi: 10.1063/1.2433027

View online: <http://dx.doi.org/10.1063/1.2433027>

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Soft chemical deposition of BiFeO₃ multiferroic thin films

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(Received 27 October 2006; accepted 19 December 2006; published online 31 January 2007)

BiFeO₃ thin films free of secondary phases were obtained by the soft chemical solution on Pt(111)/Ti/SiO₂/Si substrates after annealing at 500 °C for 2 h. The film grown in the (100) direction presented a remanent polarization P_r of 31 $\mu\text{C}/\text{cm}^2$ at room temperature. Electrical measurements using both quasistatic hysteresis and pulsed polarization confirm the existence of ferroelectricity with a switched polarization of 60–70 $\mu\text{C}/\text{cm}^2$, $\Delta P = (P^* - P)$. Low leakage conduction and an out-of-plane piezoelectric (d_3) coefficient of 40 pm/V were obtained by the improvement of preparation technology. © 2007 American Institute of Physics.
[DOI: 10.1063/1.2433027]

Ferroelectromagnets are the class of materials exhibiting coexistence of magnetic and ferroelectric orderings in a certain range of temperature.¹ These materials, therefore, not only can be used in magnetic and ferroelectric devices but also have the potential ability to couple the electric and magnetic polarizations, providing an additional degree of freedom in device design and applications. Consequently, ferroelectromagnetism becomes the subject of intensive investigations because these materials potentially offer a whole range of applications, including the emerging field of spintronics, data-storage media,² and multiple-state memories.³

It is known that relatively few multiferroic materials exist as naturally occurring phases, examples of which include BiFeO₃, BiMnO₃, BiCrO₃, etc.⁴ Recently, BiFeO₃ (BFO) multiferroics have drawn a great deal of attention due to their superior ferroelectric properties in epitaxial thin film form in comparison to counterpart bulk single crystals or ceramics.^{5–9} Although the origin of enhancement of the ferroelectric and ferromagnetic responses is not clearly understood, the possibility of a high value of remanent polarization ($P_r \sim 55 \mu\text{C}/\text{cm}^2$) and magnetization ($M_s \sim 80 \text{ emu/cc}$) in (001) BiFeO₃ thin films ($\sim 70 \text{ nm}$) opens an avenue to study the host BiFeO₃ for various functional device applications.¹⁰ It is quite desirable to obtain large polarization properties at low temperatures. In this regard, a viable manufacturable process (such as a chemical solution deposition) is required for the deposition of the ferroelectric layer. The polymeric precursor method has a suitable potential for technological applications because of their precise control of composition and homogeneity and good conformality.¹¹ However, there is no report about the piezoelectric behavior of BFO thin films deposited on Pt(111)/Ti/SiO₂/Si substrates by the polymeric precursor method.

In this letter, we present the preparation of BFO films on Pt(111)/Ti/SiO₂/Si substrates with excellent structural, microstructural, and electrical properties by the polymeric precursor method. Iron (III) nitrate nonahydrate, 99.5% purity (Merck), and bismuth nitrate, 99.5% purity (Aldrich), were used as raw materials. The precursor solutions of bismuth and iron were prepared by adding the raw materials to ethylene glycol and concentrated aqueous citric acid under heating and stirring. Appropriate quantities of solutions of Fe and Bi were mixed and homogenized by stirring at 90 °C. An excess of 5 wt % Bi was added to the solution, aiming to minimize the bismuth loss during annealing. Without bismuth addition, single phase BFO thin film could not be obtained. The molar ratio of metal/citric acid/ethylene glycol was 1/4/16. The viscosity of the resulting solution was adjusted to 20 cP by controlling the water content using a Brookfield viscosimeter. The films were spin coated from a BFO deposition solution onto Pt(111)/Ti/SiO₂/Si substrates. The BFO films were completely crystallized after annealing at 500 °C for 2 h. Multilayered films were obtained by spinning ten times the deposition solution on the surface of the substrate at 5000 rpm.

Phase analysis of the films was performed at room temperature by x-ray diffraction (XRD) patterns recorded on a Rigaku-DMAX 2000PC with Cu-K α radiation in the 2θ range from 20°–60° with 0.3°/min. The thickness of the annealed thin film was determined using scanning electron microscopy (Topcom SM-300) by looking at the transversal section. In this case, backscattered electrons were utilized. Three measurements were done to obtain an average value of thickness. A PHI-5702 multifunction x-ray photoelectron spectrometer (XPS) was used, working with an Al-K α x-ray source of 29.35 eV passing energy. The pressure in the chamber during the experiments was about 4.5×10^{-9} Torr. The calibration of binding energy scale was controlled using the O 1s line, which appears in the photoelectron spectra of the as-grown samples. The surface morphology of BFO thin films was

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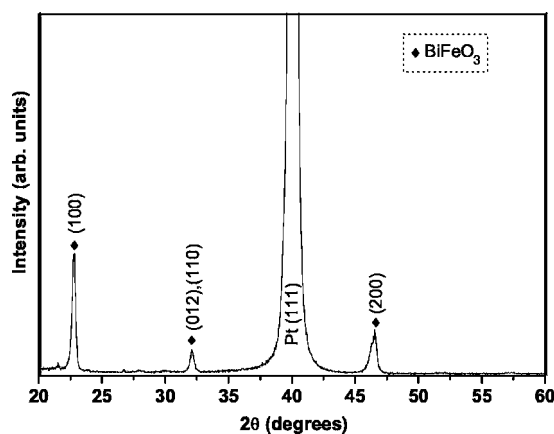


FIG. 1. X-ray diffraction of BFO thin films annealed at 500 °C for 2 h in static air.

measured by atomic force microscopy (AFM) using tapping mode technique. Next, a 0.5 mm diameter top Au electrode was sputtered through a shadow mask at room temperature. After deposition of the top electrode, the film was subjected to a postannealing treatment in a tube furnace under oxygen atmosphere at 300 °C for 1 h. Here, the desired effect was to decrease eventually the present oxygen vacancies.

The ferroelectricity was investigated using a Sawyer-Tower circuit attached to a computer-controlled standardized ferroelectric test system (Radiant Technology 6000 A). Out-of-plane piezoelectric response measurements using piezoelectric force microscopy (PFM) were performed to study the piezoelectric properties of these films. The films were first poled at a negative dc bias (−12 V) applied to a conducting probe while scanning over a $2 \times 2 \mu\text{m}^2$ area. Another poling was performed, with the probe biased at the opposite voltage (+12 V) during scanning over a $1 \times 1 \mu\text{m}^2$ area inside the previously poled one. Details on the PFM technique can be found in our previous work.¹¹

Figure 1 displayed the XRD pattern of BFO thin films annealed at 500 °C for 2 h. As can be seen, a single perovskite phase free of impurities was obtained. The diffraction peaks were identified using the pseudocubic structure. The intensities of (100) and (200) diffraction peaks were stronger with respect to that of the (110) peak.

In order to identify the chemical bonding of BFO thin films, we performed XPS studies. The wide-range spectrum of BFO thin films deposited is shown in Fig. 2(a). The spectrum expanded from 700 to 745 eV is also shown in Fig. 2(b). The 3/2 and 1/2 spin-orbit doublet components of the Fe 2p photoemission located at 711.1 and 724.6 eV, respectively, were identified as Fe³⁺. No Fe²⁺ and Fe were found. The XPS results show that BFO thin film has a single phase with a Fe³⁺ valence state, consistent with the XRD result shown in Fig. 1. The oxidation state of Fe was purely 3+, which was advantageous for producing BFO film with low leakage.

The room temperature P - E hysteresis loops of BFO thin film are shown in Fig. 3(a). The film presents well-saturated hysteresis characteristics with a remanent polarization (P_r) of $31 \mu\text{C}/\text{cm}^2$ and a coercive field (E_c) of 560 kV/cm at a maximum applied electric field of 1000 kV/cm. We attribute the value of our P_r to the intense (100) preferred orientation. According to Wang et al.,⁹ the ferroelectricity of BFO originates from the relative displacements of Bi ion and Fe-O

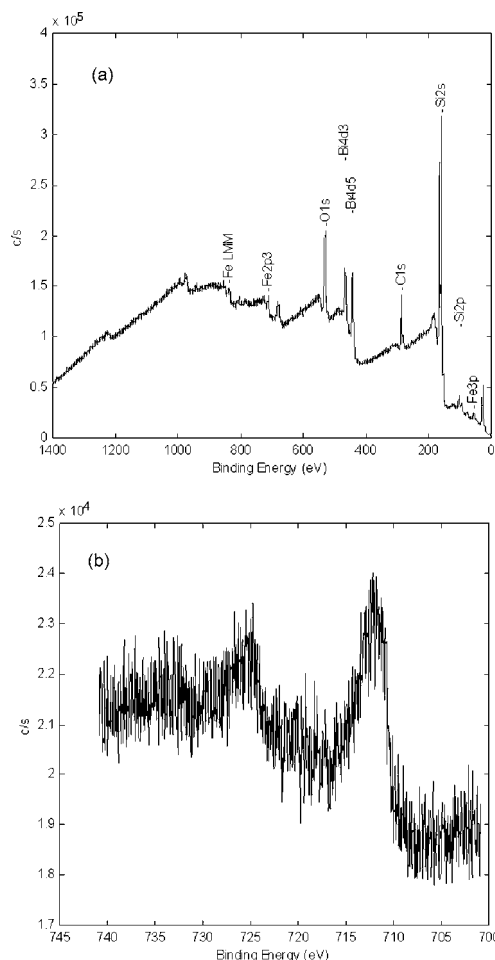


FIG. 2. XPS analysis of BFO thin films annealed at 500 °C for 2 h in static air: (a) wide-range spectrum and (b) Fe 2p peaks.

octahedron along the (111) orientation in epitaxial BFO thin films and the projection polarization along the (110) orientation is larger than that of the (100) orientation. Since our films are intense (100) we reasonably did not expect a larger polarization. A high coercive field is probably originated from the small grain size (140 nm) of the BFO thin films, since the polarization switching is usually more difficult in films with fine grains. In order to extract the real switched polarization properties, PUND measurements [$\Delta P = P^*$ (switched polarization) $-\bar{P}$ (nonswitched polarization)] were also performed and the result is shown in Fig. 3(b). The obtained switched polarization ΔP is $60\text{--}70 \mu\text{C}/\text{cm}^2$ which is consistent with the $2P_r$ value from the P - E hysteresis loop. The switched polarization values of $\sim 60 \mu\text{C}/\text{cm}^2$ were observed, which began to saturate at $600\text{--}650 \text{ kV}/\text{cm}$. Moreover, the polarization showed weak pulse width dependence in the range of $1 \mu\text{s}$ – 1 ms , as shown in Fig. 3(c). This demonstrates that the measured polarization switching is an intrinsic property of BFO thin films and is not dominated by leakage, which was a critical obstacle in determining the ferroelectric property of bulk BFO.⁸

The d_{33} (V) hysteresis loop is also given in Fig. 4(a). An out-of-plane piezoelectric coefficient of 40 pm/V was measured at room temperature. As can be seen, the hysteresis loop shows an offset in the vertical direction which can be caused by nonswitchable domains pinned near the electrode-film interface.¹² A vertical shift in the d_{33} hysteresis loop can also be associated with a built-in electric field at the bottom

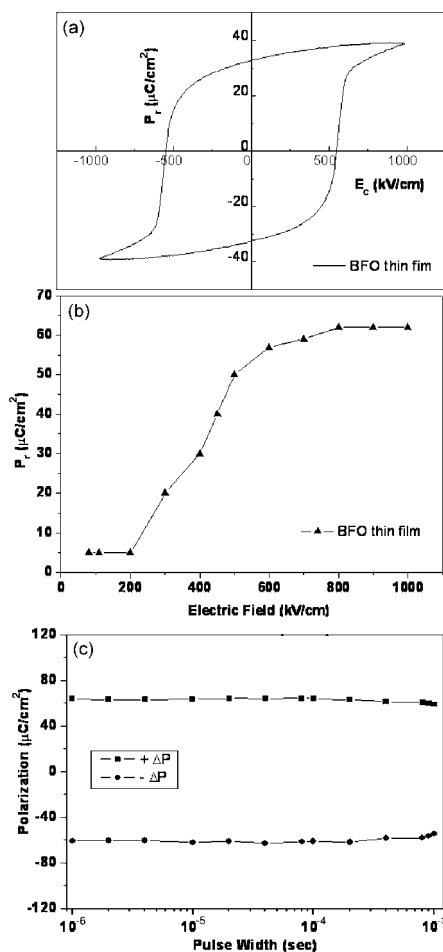


FIG. 3. (a) Remanent polarization-drive voltage hysteresis loops, (b) pulsed polarization (ΔP) as a function of an applied voltage and (c) pulse width dependence of switched polarization (ΔP) in the range of 1 μs –1 ms for BFO thin films annealed at 500 °C for 2 h in static air.

interface, mechanical stress from the tip, etc.¹³ Although the remanent d_{33} value obtained was less than that of the epitaxial BFO thin films, perhaps because of tensile stress and the size effect of the ferroelectric materials, it is high for polycrystalline ferro/piezoelectric films. The surface morphology of BFO thin films measured by AFM is shown in Fig. 4(b). A flat surface with a surface roughness of 2 nm was observed within the area of $3 \times 3 \mu\text{m}^2$ on 300-nm-thick film. Figure 4(c) shows the out-of-plane piezoresponse image of the as-grown films after applying a bias of +12 V, on an area of $2 \times 2 \text{ mm}^2$, and then an opposite bias of -12 V, in the central $1 \times 1 \text{ mm}^2$ area. To obtain the domain images of the BFO thin films, a high voltage in order to exceed the coercive field was applied during scanning. The contrast in these images is associated with the direction of the polarization.¹³ The white regions in the out-of-plane PFM images correspond to domains with the polarization vector oriented toward the bottom electrode hereafter referred to as down polarization, while the dark regions correspond to domains oriented upward referred to as up polarization. Grains which exhibit no contrast change are associated with zero out-of-plane polarization. This can be concluded from the piezocontrast given by the as-grown state.

In summary, we have demonstrated a viable chemical deposition process, which enables the growth of good quality BiFeO₃ multiferroic thin films. The leakage-current density

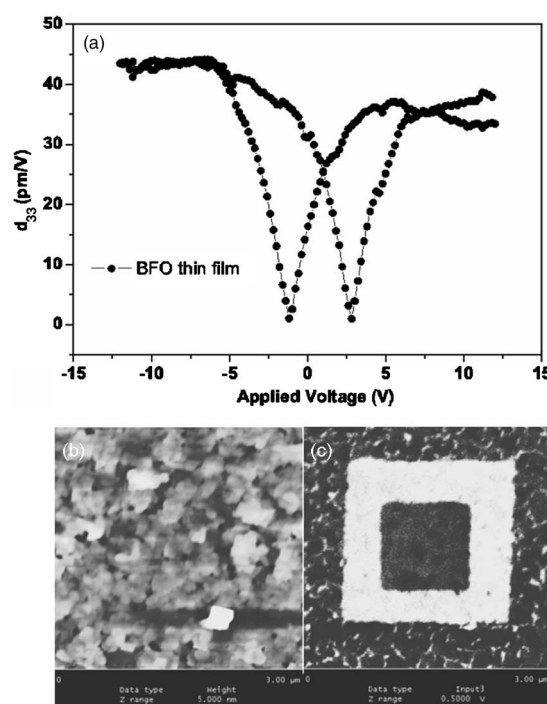


FIG. 4. (a) Piezoelectric coefficient loop d_{33} , of a 300-nm-thick BiFeO₃, (b) surface morphology of BiFeO₃ thin films ($3 \times 3 \mu\text{m}^2$) measured by AFM, and (c) out-of-plane PFM image of BFO thin films annealed at 500 °C for 2 h in static air.

of the film was around $10^{-7} \text{ A}/\text{cm}^2$ with a remanent polarization P_r of $31 \mu\text{C}/\text{cm}^2$ at room temperature. Our results indicate that the BFO films exhibit a good piezoelectric response of 40 pm/V. For practical applications, there are some drawbacks, which should be overcome as a reduction in the coercive field and in the leakage-current density. These require a careful study of the defect chemistry of the films as well as annealing in oxygen ambient and substitution of Bi site for an isovalent ion.

The authors thank Prof. Hess of Georgia Institute of Technology for the XPS.

- ¹E. K. H. Salje, *Phase Transformations in Ferroelastic and Co-elastic Solids* (Cambridge University Press, Cambridge, 1990).
- ²M. Fiebig, Th. Lottermoser, D. Fröhlich, A. V. Golsev, and R. V. Pisarev, *Nature* (London) **419**, 819 (2002).
- ³N. Hill, *J. Phys. Chem. B* **104**, 6694 (2000).
- ⁴G. A. Smolenskii and I. E. Chupis, *Usp. Fiz. Nauk* **25**, 475 (1982).
- ⁵J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, *Science* **299**, 1719 (2003).
- ⁶J. Li, J. Wang, M. Wuttig, R. Ramesh, N. Wang, B. Ruetter, A. P. Pyatakov, A. K. Zvezdin, and D. Viehland, *Appl. Phys. Lett.* **84**, 5261 (2004).
- ⁷C. Ederer and N. A. Spaldin, *Phys. Rev. B* **71**, 224103 (2005).
- ⁸J. R. Teague, R. Gerson, and W. J. James, *Solid State Commun.* **8**, 1073 (1970).
- ⁹Y. P. Wang, L. Zhou, M. F. Zhang, X. Y. Chen, J. M. Liu, and Z. G. Liu, *Appl. Phys. Lett.* **84**, 1731 (2004).
- ¹⁰J. Wang, A. Scholl, H. Zheng, S. B. Ogale, D. Viehland, D. G. Schlom, N. A. Spaldin, K. M. Rabe, M. Wuttig, L. Mohaddes, J. Neaton, U. V. Waghmare, T. Zhao, and R. Ramesh, *Science* **307**, 1203 (2005).
- ¹¹A. Z. Simões, M. A. Ramírez, A. Ries, E. Longo, J. A. Varela, and R. Ramesh, *Appl. Phys. Lett.* **88**, 072916 (2006).
- ¹²A. L. Kholkin, E. L. Colla, A. K. Tagantsev, D. V. Taylor, and N. Setter, *Appl. Phys. Lett.* **68**, 2577 (1996).
- ¹³A. Gruverman, O. Auciello, and H. Tokumoto, *Annu. Rev. Mater. Sci.* **28**, 101 (1998).