

Piezoelectric behavior of SrRuO₃ buffered lanthanum modified bismuth ferrite thin films grown by chemical method

A. Z. Simões, A. H. M. Gonzalez, E. C. Aguiar, C. S. Riccardi, E. Longo et al.

Citation: *Appl. Phys. Lett.* **93**, 142902 (2008); doi: 10.1063/1.2979692

View online: <http://dx.doi.org/10.1063/1.2979692>

View Table of Contents: <http://apl.aip.org/resource/1/APPLAB/v93/i14>

Published by the AIP Publishing LLC.

Additional information on *Appl. Phys. Lett.*

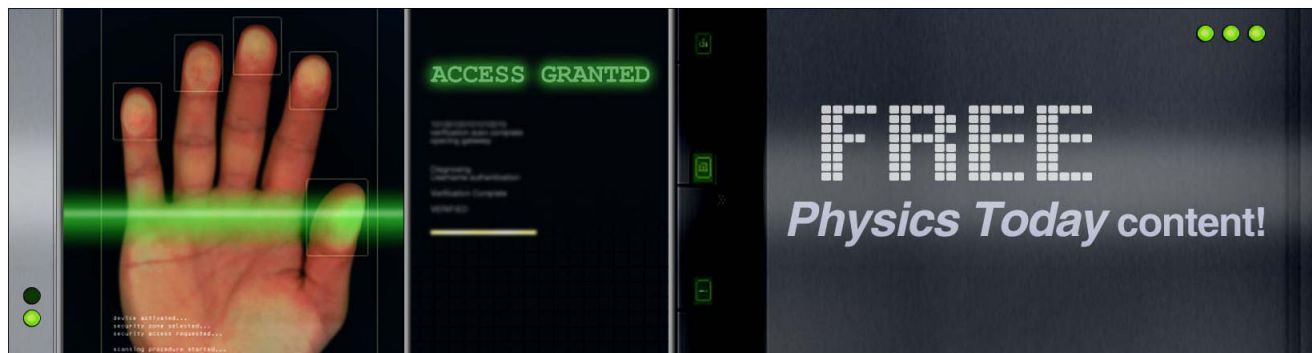
Journal Homepage: <http://apl.aip.org/>

Journal Information: http://apl.aip.org/about/about_the_journal

Top downloads: http://apl.aip.org/features/most_downloaded

Information for Authors: <http://apl.aip.org/authors>

ADVERTISEMENT



Piezoelectric behavior of SrRuO₃ buffered lanthanum modified bismuth ferrite thin films grown by chemical method

A. Z. Simões,^{1,a)} A. H. M. Gonzalez,¹ E. C. Aguiar,² C. S. Riccardi,² E. Longo,² and J. A. Varela²

¹Faculdade de Ciências, Departamento de Química, Universidade Estadual Paulista,

Av. Luiz Edmundo Carrijo Coube, 14-01, Vargem Limpa, 17033-360 Bauru, São Paulo, Brazil

²Laboratório Interdisciplinar em Cerâmica, Instituto de Química, Universidade Estadual Paulista, P.O. Box 355, 14801-907 Araraquara, São Paulo, Brazil

(Received 23 July 2008; accepted 14 August 2008; published online 7 October 2008)

Lanthanum modified bismuth ferrite thin film (BLFO) of pure perovskite phase was deposited on SrRuO₃-buffered Pt/TiO₂/SiO₂/Si (100) substrates by soft chemical method. (111)-preferred oriented BLFO film was coherently grown at a temperature of 500 °C. The crystal structure of the film was characterized by using x-ray diffraction. The spontaneous polarization of the film was 25 μC/cm². The film has a piezoelectric coefficient d_{33} equal to 85 pm/V and a weak pulse width dependence indicating intrinsic ferroelectricity. Retention measurement showed no decay of polarization while piezoelectric response was greatly improved by the conductor electrode. © 2008 American Institute of Physics. [DOI: 10.1063/1.2979692]

Tremendous research activity has recently focused on understanding the science behind the coexistence of ferroelectricity and ferromagnetism within a single multifunctional material^{1,2} that would allow the realization of additional functionalities in electronic and magnetic devices. Bismuth ferrite (BFO) possesses large polarization values and low crystallization temperatures, both of which are desirable properties for high density ferroelectric random access memory.³⁻⁶ Application of the Pt layer as the bottom electrode provides low resistivity and high temperature stability, but some disadvantages have been observed, including deterioration of ferroelectric properties by interdiffusion with the interposed adhesion layer of Ti on the substrate, formation of hillocks, and formation of dead layers at interfaces. Conductive oxide layers as electrodes were confirmed to be a good alternative in solving these problems.^{7,8} Recently, some researchers prepared BFO thin films on Pt coated silicon substrate using the pulsed laser deposition (PLD) method. The PLD and liquid phase epitaxy (LPE) methods were also used to grow BFO thin films on SrTiO₃ (STO) substrate with SrRuO₃ (SRO) layer in which the conducting oxide SRO layer was used as both the bottom electrode and the buffer layer.⁹⁻¹¹

It is well known that perovskite oxide electrode, such as SRO, LaNiO₃, and BaPbO₃, effectively improved crystal growth and electric properties of ferroelectric oxide.^{7,8,12-14} Wang *et al.*¹⁵ reported the considerable enhancement in the leakage, ferro/piezoelectric, and magnetic properties of the epitaxial BFO films with conductive SRO oxide electrodes. Of particular interest, the SRO electrode is promising in inducing the preferred orientation and improving the film/electrode interface of ferroelectric films. Previous studies suggested that the fatigue endurance can be effectively suppressed by La doping.¹⁶ To our knowledge, few reports are available on the retention characteristics of lanthanum modified bismuth ferrite thin film (BLFO) on an oxide electrode. Therefore, we investigated the role exerted by the bottom

electrode in polarization switching and ferroelectric reliability of BLFO films crystallized by the soft chemical method.

The SRO and BLFO thin films were prepared using the polymeric precursor method, as described elsewhere.¹⁷ The bottom electrode thin films were spin coated on Pt/Ti/SiO₂/Si (100) substrates by a commercial spinner operating at 5000 rpm for 30 s (spin coater KW-4B, Chemat Technology). Each layer was pre-fired at 400 °C for 2 h in a conventional oven. After the pre-firing, each layer was crystallized in a microwave furnace at 700 °C for 10 min. Using the same procedure, the BLFO thin films were deposited by spinning the precursor solution on the desired substrates. Through this process, we have obtained thickness values of about 150 nm (five layers) for the bottom electrode and around 300 nm for BLFO (ten layers), reached by repeating the spin coating and heating treatment cycles. The microwave furnace used to crystallize the SRO electrode was a simple domestic model similar to that described in literature.¹⁸ Phase analyses of the films were performed at room temperature by x-ray diffraction (XRD) using a Bragg-Brentano diffractometer (Rigaku 2000) and Cu K α radiation. 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. Calibration of binding energy scale was controlled using the O 1s line, which appears in the photoelectron spectra of the as grown samples. The electric properties of Pt/BLFO/SRO/Pt/Ti/SiO₂/Si (100) capacitor structure were measured. The upper electrodes of Pt for the electrical measurements were prepared by evaporation through a shadow mask with a 0.2 mm² dot area. Dielectric and ferroelectric properties of the capacitor were measured using HP 4192A impedance/gain phase analyzer and a Radiant Technology RT6000 A in a virtual ground mode, respectively.

Figure 1 shows the XRD pattern of BLFO deposited on SRO electrode. The film consists of (111)-oriented films and exhibits a pure perovskite phase. Furthermore, except for the Si (100) and Pt (111) peaks, no peaks of impure phases such

^{a)}Electronic mail: alezipo@yahoo.com.

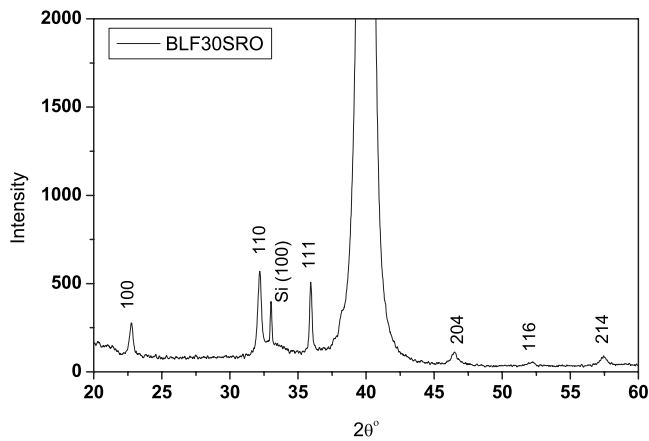


FIG. 1. XRD of BLFO thin film deposited on SRO electrode and annealed at 500 °C in static air for 2 h.

as $\text{Bi}_2\text{Fe}_4\text{O}_9$ and $\text{Bi}_{46}\text{Fe}_2\text{O}_{72}$ were spotted so pure phase BiFeO_3 films were obtained by the soft chemical method. The (111) orientation can be attributed to the differences in nucleation energy between the ferroelectromagnetic material and the oxide electrode.

In order to identify the chemical bonding of BFO thin films, we performed XPS studies. The spectrum expanded from 700 to 745 eV, as shown Fig. 2. The $\frac{3}{2}$ and $\frac{1}{2}$ spin-orbit doublet components of the Fe $2p$ photoemission located at 711.1 and 724.6 eV, respectively, were identified as Fe^{3+} . No Fe^{2+} and Fe were found. The XPS results show that BFO thin films annealed at 500 °C for 2 h have a single phase with a Fe^{3+} valence state, consistent with XRD result shown in Fig. 1. The oxidation state of Fe was purely 3+, which was advantageous in producing BFO film with low leakage.

Ferroelectric properties were characterized using both polarization hysteresis and pulsed polarization measurements. Figure 3(a) shows a set of hysteresis loops measured at a frequency of 60 Hz. A remnant polarization of $P_r = 25 \mu\text{C}/\text{cm}^2$ is observed, which is smaller than that of films grown on single crystal STO substrates ($\sim 55 \mu\text{C}/\text{cm}^2$ on [100] STO and $\sim 95 \mu\text{C}/\text{cm}^2$ on [111] STO).¹⁹ This can be understood as a consequence of the smaller c/a ratio of

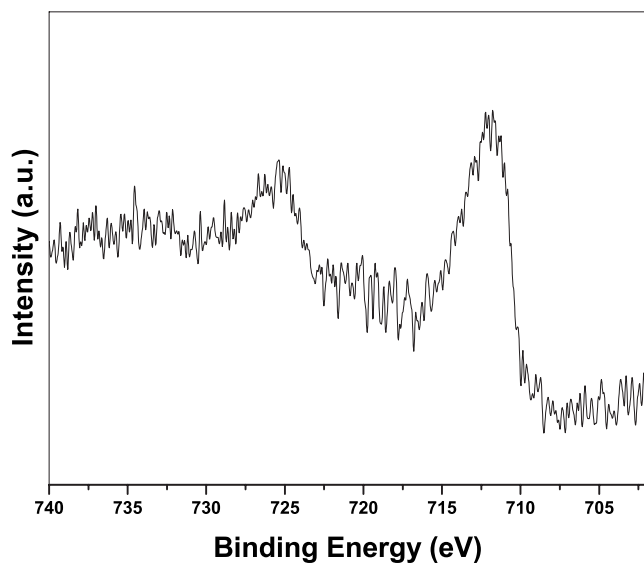


FIG. 2. XPS analysis of BLFO thin films deposited on SRO electrode and annealed at 500 °C in static air for 2 h.

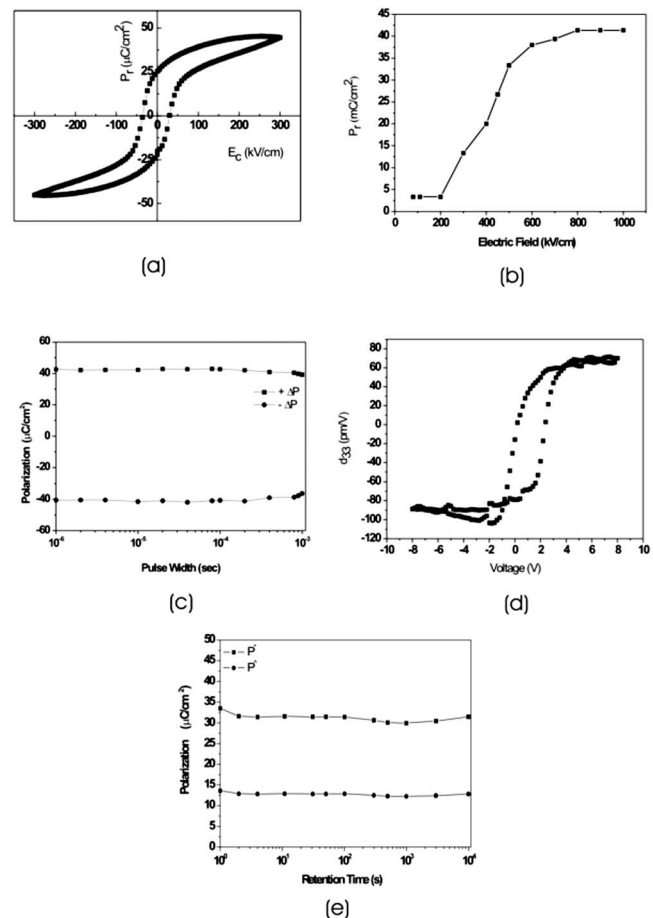


FIG. 3. (a) Remanent polarization-electric field hysteresis loops, (b) pulsed polarization (ΔP) as a function of an applied voltage, and (c) pulse width dependence of switched polarization (ΔP) in the range from 1 μs to 1 ms. (d) Piezoelectric coefficient loop d_{33} and (e) retention characteristics for BLFO thin film deposited on SRO electrode and annealed at 500 °C in static air for 2 h.

BLFO on SRO. To more closely investigate the ferroelectric properties, polarization positive up negative down (PUND) measurements [$\Delta P = P^*$ (switched polarization), \hat{P} (non-switched polarization)] were also performed and the result is shown in Fig. 3(b). The obtained switched polarization ΔP is 38–42 $\mu\text{C}/\text{cm}^2$, which is consistent with the $2P_r$ value from the P - E hysteresis loop. The switched polarization values of $\sim 40 \mu\text{C}/\text{cm}^2$ were observed, which began to saturate at 600–650 kV/cm. Pulse polarization measurements that are less likely convoluted by leakage and nonlinear dielectric effects confirmed this result. Also, note the weak pulse width dependence in Fig. 3(c) once saturation is reached, which is yet another indication of robust intrinsic ferroelectricity. This demonstrates that the measured polarization switching is an intrinsic property of BLFO thin films and is not dominated by leakage, which was a critical obstacle in determining the ferroelectric property of bulk BFO.²⁰ For use in memory applications, the coercive field (which is currently 2–3 V for a 200 nm film) has to be lowered to about 0.7–1 V. Our preliminary experiments using La substitution suggest a similar prospect in the BFO system. The d_{33} (V) hysteresis loop is shown in Fig. 3(d). The maximum d_{33} value of $\sim 80 \text{ pm}/\text{V}$ is better than the reported value for a BFO deposited on Si.⁹ The enhancement of polarization could be caused by the (111) orientation of the ferroelectric film de-

posited on SRO oxide, which reduces the initial nucleation rate when crystallizing the film. The presented value reported for our BLFO film suggests that this material can be considered as a viable alternative for lead-free piezoelectric devices. The stability of the polar state is confirmed by retention measurements as shown in Fig. 3(e). The overall retention time dependence of polarization retention for the BLFO film is quite good. After a retention time of 1×10^4 s, the polarization loss was only about 8.0% of the value measured at $t=1.0$ s for a 9 V applied voltage. For the infant period (within 10 s), depolarization fields could be the main contribution to polarization loss. Similar retention loss behavior has been reported for $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ deposited on Pt/TiO₂/SiO₂/Si.²¹ Note that greater than 40% retention loss is often observed for various ferroelectric thin films after 10^4 s even at room temperature.²² Such behavior has been attributed to a depolarization field, which can exist due to the incomplete compensation between the polarization charge and the free charge in the electrodes.

In summary, BLFO thin films were deposited on the SRO/Pt/TiO₂/SiO₂/Si (100) substrates by the chemical solution deposition method. The BLFO thin film showed a remanent polarization (P_r) of 25 $\mu\text{C}/\text{cm}^2$ at room temperature. Retention failure tests pointed to that the BLFO films have quite good long-time retention characteristics, retaining 92% of the values measured at $t=1$ s. These results indicate that SRO is an effective oxide electrode to obtain good ferroelectric BLFO thin films. Furthermore, it was clearly demonstrated that the good piezoelectric BLFO thin films could be fabricated by a chemical solution deposition method, which is advantageous for real device applications.

The authors gratefully acknowledge the financial support of the Brazilian agencies FAPESP, CNPq, and CAPES and Dr. Hess of Georgia Institute of Technology for XPS facilities.

- ¹N. A. Hill, *J. Phys. Chem. B* **104**, 6694 (2000).
- ²T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, *Nature (London)* **426**, 55 (2003).
- ³J. Wang, H. Zheng, Z. Ma, S. Prasertchoung, M. Wuttig, R. Droopad, J. Yu, K. Eisenbeiser, and R. Ramesh, *Appl. Phys. Lett.* **85**, 2574 (2004).
- ⁴Y. H. Lee, J. M. Wu, and C. H. Lai, *Appl. Phys. Lett.* **88**, 042903 (2006).
- ⁵S. K. Singh and H. Ishiwara, *Jpn. J. Appl. Phys., Part 2* **44**, L734 (2005).
- ⁶C. C. Lee, J. M. Wu, and C. P. Hsiung, *Appl. Phys. Lett.* **90**, 182909 (2007).
- ⁷C. S. Liang, J. M. Wu, and M. C. Chang, *Appl. Phys. Lett.* **81**, 3624 (2002).
- ⁸M. S. Chen, T. B. Wu, and J. M. Wu, *Appl. Phys. Lett.* **68**, 1430 (1996).
- ⁹J. Wang, J. B. Neaton, H. Zheng, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, *Science* **299**, 1719 (2003).
- ¹⁰X. D. Qi, J. H. Dho, R. Tomov, M. G. Blamire, and J. L. MacManus-Driscoll, *Appl. Phys. Lett.* **86**, 062903 (2005).
- ¹¹X. D. Qi, M. Wei, Y. Lin, Q. Jia, D. Zhi, J. H. Dho, M. G. Blamire, and J. L. MacManus-Driscoll, *Appl. Phys. Lett.* **86**, 071913 (2005).
- ¹²B. Nagaraj, S. Aggarwal, and R. Ramesh, *J. Appl. Phys.* **90**, 375 (2001).
- ¹³C. C. Yang, M. S. Chen, T. J. Hong, C. M. Wu, J. M. Wu, and T. B. Wu, *Appl. Phys. Lett.* **66**, 2643 (1995).
- ¹⁴Y. R. Luo and J. M. Wu, *Appl. Phys. Lett.* **79**, 3669 (2001).
- ¹⁵J. 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).
- ¹⁶A. Z. Simões, L. S. Cavalcante, C. S. Riccardi, J. A. Varela, and E. Longo, *Curr. Appl. Phys.* (in press).
- ¹⁷A. Z. Simões, M. A. Ramirez, C. S. Riccardi, E. Longo, and J. A. Varela, *Mater. Lett.* **60**, 2020 (2006).
- ¹⁸A. Z. Simões, M. A. Ramirez, A. Ries, F. Wang, E. Longo, and J. A. Varela, *Mater. Res. Bull.* **41**, 1461 (2006).
- ¹⁹J. F. 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).
- ²⁰J. R. Teague, R. Gerson, and W. J. James, *Solid State Commun.* **8**, 1073 (1970).
- ²¹B. S. Kang, J.-G. Yoon, T. K. Song, S. Seo, Y. W. So, and T. W. Noh, *Jpn. J. Appl. Phys., Part 1* **41**, 5281 (2002).
- ²²J. W. Hong, W. Jo, D. C. Kim, S. M. Cho, H. J. Nam, H. M. Lee, and J. U. Bu, *Appl. Phys. Lett.* **75**, 3183 (1999).