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S. Y. Yang, F. Zavaliche, L. Mohaddes-Ardabili, V. Vaithyanathan, D. G. Schlom, Y. J. Lee, Y. H. Chu, M. P. Cruz, Q. Zhan, T. Zhao, and R. Ramesh

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Metalorganic chemical vapor deposition of lead-free ferroelectric BiFeO₃ films for memory applications

S. Y. Yang,^{a)} F. Zavaliche, and L. Mohaddes-Ardabili

Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742

V. Vaithyanathan and D. G. Schlom

Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania 16802

Y. J. Lee, Y. H. Chu, M. P. Cruz,^{b)} Q. Zhan, T. Zhao, and R. Ramesh

Department of Materials Science and Engineering and Department of Physics, University of California, Berkeley, California 94720

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We have grown BiFeO₃ thin films on SrRuO₃/SrTiO₃ and SrRuO₃/SrTiO₃/Si using liquid delivery metalorganic chemical vapor deposition. Epitaxial BiFeO₃ films were successfully prepared through the systematic control of the chemical reaction and deposition process. We found that the film composition and phase equilibrium are sensitive to the Bi:Fe ratio in the precursor. Fe-rich mixtures show the existence of α -Fe₂O₃, while Bi-rich mixtures show the presence of β -Bi₂O₃ as a second phase at the surface. In the optimized films, we were able to obtain an epitaxial single perovskite phase thin film. Electrical measurements using both quasistatic hysteresis and pulsed polarization measurements confirm the existence of ferroelectricity with a switched polarization of 110–120 $\mu\text{C}/\text{cm}^2$, $\Delta P(=P^* - \hat{P})$. Out-of plane piezoelectric (d_{33}) measurements using an atomic force microscope yield a value of 50–60 pm/V. © 2005 American Institute of Physics.

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There is currently significant interest in the field of ferroelectric thin film materials and devices, with a strong focus on the integration of thin films on Si-complementary metal-oxide semiconductor (CMOS) for nonvolatile memory (FeRAM) applications. Ferroelectric perovskites, namely the lead zirconate titanate (PZT), strontium bismuth tantalite (SBT), and bismuth titanate (BIT) family of materials have emerged as the most attractive candidates for the storage capacitor layer. Although considerable progress towards integration is being made, there are some key questions that are pertinent to these materials systems. The optimum processing temperatures are still quite high for the SBT system, although the recent progress in reducing the temperature is very encouraging;^{1,2} in the case of the PZT system, the inherent toxicity of lead is of great concern. Therefore, it is quite desirable to have a ferroelectric material system that has the large polarization properties and low temperature processability of the PZT system with the chemical “benignness” of the SBT and BIT system.

In this regard, recently we have reported a significant ferroelectric polarization in epitaxial thin films of the lead-free perovskite, bismuth ferrite (BFO).^{3,4} In the process of exploring the viability of using this materials system as an alternative ferroelectric system that embodies the positive attributes of both the PZT and SBT systems into a FRAM memory process flow, it is imperative that a viable, manufacturable process (such as a chemical vapor deposition) be available for the deposition of the ferroelectric layer. In this

letter, we describe such a process which has enabled us to obtain high quality BFO films. We describe the precursor chemistry, the process window, as well as the ferroelectric and piezoelectric properties of films deposited on single crystal (001) SrTiO₃ (STO) and STO/Si covered with an SrRuO₃ (SRO) electrode layer.

A metalorganic chemical vapor deposition (MOCVD) equipped with liquid delivery system was used with Tris(2,2,6,6-tetramethyl-3,5-heptanedionate)bismuth (III) [Bi(thd)₃] and Tris(2,2,6,6-tetramethyl-3,5-heptanedionate)iron (III) [Fe(thd)₃] dissolved in tetrahydrofuran which are both based on β -diketonates as the liquid metalorganic precursor materials. Their intrinsic similarity in organometallic chemistry makes them reasonably compatible. We use a showerhead that is designed to be heated with oil to avoid condensation of vaporized precursors and achieve high uniform film deposition over a 2 in. substrate. The system has 13 heating controllers that adjust the temperature downstream from the vaporizer and enables us to obtain a thermally stable growth condition.

Consistent with our previous work on CVD process of PZT thin films, we found that the film composition and structure are quite sensitive to the substrate temperature, the precursor delivery ratio as well as the vaporizer temperature.⁵ The variation of film composition with different precursor supply ratios is shown in Fig. 1(a). The volumetric liquid source supply mixing ratio of Bi/(Bi+Fe) was changed from 0.50 to 0.85 and growth temperature was set at 650 °C. We note that the mixing ratio represents the volumetric ratio of liquid sources at room temperature, and not the actual gas mixing ratio in the reactor. A stoichiometric composition was obtained from a Bi/(Bi+Fe) liquid source mixing ratio of 0.70. The high supply ratio of Bi precursor with respect to Fe

^{a)}Electronic mail: syyang@wam.umd.edu

^{b)}Also at: Centro de Ciencias de la Materia Condensada (CCMC)-UNAM. Km. 107 Carretera Tijuana-Ensenada. Ensenada, B.C., Mexico, Codigo Postal 22800.

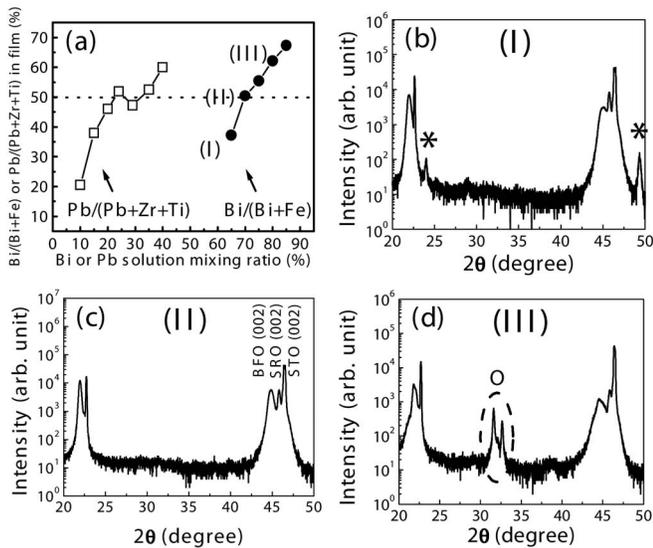


FIG. 1. (a) Relation between Bi and Fe atomic percentage in BiFeO_3 films as measured by Rutherford backscattering and energy dispersive spectrometry, for precursor mixing ratio prepared at growth temperature of 650°C . Atomic percentage ratio in $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (from Ref. 6) is also plotted at the same scale for comparison. θ - 2θ x-ray diffraction scans for (b) Fe-rich phase (*: $\alpha\text{-Fe}_2\text{O}_3$), (c) stoichiometric composition, and (d) Bi-rich phase (○: $\beta\text{-Bi}_2\text{O}_3$).

precursor required to achieve stoichiometric composition in films can be understood as a consequence of the low vapor pressure of $\text{Bi}(\text{thd})_3$ as compared with $\text{Fe}(\text{thd})_3$. At a temperature of 190°C , the vapor pressure of $\text{Fe}(\text{thd})_3$ is about 2.5 times higher than that of $\text{Bi}(\text{thd})_3$. In addition, $\text{Bi}(\text{thd})_3$ is not completely vaporized and leaves $\sim 30\%$ residue which is not volatile as deduced from thermogravimetric analysis. The incomplete vaporization of $\text{Bi}(\text{thd})_3$ may require the high supply ratio of the Bi precursor. The change of Pb atomic content ratio which is obtained from our previous PZT process performed at the same growth temperature (650°C) is also plotted in Fig. 1(a).⁵ Here, we note that the growth window of BFO films appears to be much smaller than that of PZT as can be seen in Fig. 1(a). The composition change in the $\text{Bi}/(\text{Bi}+\text{Fe})$ ratio shows an almost linear behavior with the liquid source mixing ratio, while there is a relatively wide plateau region for the PZT film growth process. This is generally explained by a “Pb self-regulating” mechanism at high temperature growth processes and is used as the growth window.^{6,7}

Crystal structures for different composition films were determined by a typical θ - 2θ x-ray diffraction scan. Only (00 l) diffraction peaks from BFO, SRO, and STO without any second phase were observed for films with the stoichiometric composition [Fig. 1(c)]. The out-of plane lattice parameter calculated from the (002) peak of a 150 nm-thick BFO film is 4.03 \AA . This value is larger than bulk lattice constant (3.96 \AA) because of the in-plane compressive strain induced by the substrate (SRO/STO). However, additional secondary phase peaks such as (024) $\alpha\text{-Fe}_2\text{O}_3$ (Rhombohedral, $R\bar{3}c$, $a=5.112 \text{ \AA}$, $c=13.82 \text{ \AA}$) or (002) and (220) $\beta\text{-Bi}_2\text{O}_3$ (tetragonal, $P4_21c$, $a=7.741 \text{ \AA}$, $c=5.634 \text{ \AA}$) were observed in Fe- and Bi-rich films [designated as (I) and (III), respectively] in Figs. 1(b) and 1(d).

Subsequent to the optimization of the Bi:Fe ratio in the precursors, we proceeded to grow epitaxial films on single

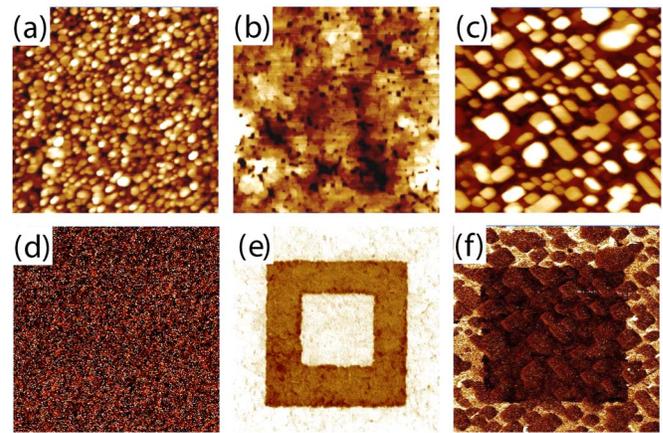


FIG. 2. (Color online) Surface morphologies of BiFeO_3 films ($3 \times 3 \mu\text{m}^2$) as measured by AFM. (a) Fe-rich, (b) stoichiometric, (c) Bi-rich BiFeO_3 films. Out-of-plane PFM images of (d) Fe-rich, (e) stoichiometric, (f) Bi-rich BiFeO_3 films. The films were successively poled at a dc bias of -8 V ($2 \times 2 \mu\text{m}^2$) and $+8 \text{ V}$ ($1 \times 1 \mu\text{m}^2$). The thickness of films is $\sim 250 \text{ nm}$.

crystalline (001) STO and (001) STO/Si. To facilitate heteroepitaxy and to introduce a conducting perovskite bottom electrode, we used a 70 nm-thick, epitaxial SRO layer deposited by pulsed laser deposition (PLD). For the electrical and electromechanical measurements, circular Pt pads with $32 \mu\text{m}$ diameter were deposited as top electrodes by a standard lift-off process.

The surface morphologies of BFO films for different compositions measured by atomic force microscopy (AFM) are shown in Figs. 2(a)–2(c). Out-of-plane piezoelectric response measurements using piezoelectric force microscopy (PFM) were performed to study the piezoelectric properties of these films, and the results are shown in Figs. 2(d)–2(f). The films were first poled at a negative dc bias (-8 V) applied to a conducting probe while scanning over a $2 \times 2 \mu\text{m}^2$ area. In the case of stoichiometric films [Fig. 2(e)], another poling was performed, with the probe biased at the opposite voltage ($+8 \text{ V}$) during scanning over a $1 \times 1 \mu\text{m}^2$ area inside the previously poled area. Details on the PFM technique can be found in our previous work.^{8,9} A flat surface with 2 nm of peak-to-peak height was observed within the area of $3 \times 3 \mu\text{m}^2$ on 250 nm-thick film with stoichiometric composition. A sharp piezoelectric response with complete reversible switching was also observed as shown in Fig. 2(e). In the case of Fe-rich films, a rough, granular surface was observed [Fig. 2(d)] and no piezoresponse was detected. On the other hand, Bi_2O_3 islands were formed on a BFO matrix in the case of Bi-rich films as shown in Figs. 3(c) and 3(f).

An out-of-plane piezoelectric coefficient, d_{33} , of 50–60 pm/V was measured at room temperature, as shown in Fig. 3(a). The P - E hysteresis loops measured at 16 kHz on the 250 nm-thick BFO film are shown in Fig. 3(b). The sharp and square loops yield a $2P_r$ value of $110\text{--}120 \mu\text{C}/\text{cm}^2$. This value is comparable to the theoretically predicted and experimentally obtained values in previous results from PLD-grown films.^{3,10} In order to extract the real switched polarization properties, PUND measurements [$\Delta P = P^*$ (switched polarization) - P' (nonswitched polarization)] were also performed to confirm these values and the result is shown in Fig. 3(c). The obtained switched polarization (ΔP) is $110\text{--}120 \mu\text{C}/\text{cm}^2$ which is consistent with the $2P_r$ value

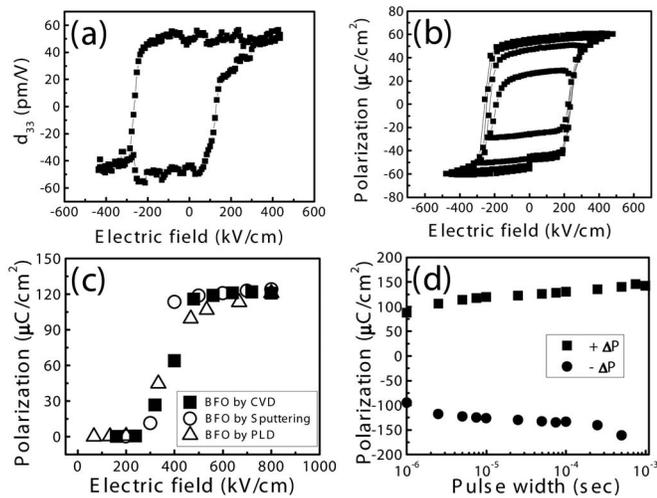


FIG. 3. (a) Piezoelectric coefficient loops, d_{33} , of a 250 nm-thick BiFeO_3 film. (b) P - E hysteresis loops of a 250 nm-thick BiFeO_3 film measured at a frequency of 16 kHz. (c) Pulsed polarization (ΔP) as a function of an applied voltage at a frequency of 16 kHz. (d) Pulse width dependence of switched polarization (ΔP) in the range from 1 μs to 1 ms at 15V.

from the P - E hysteresis loop. We compared the electric field dependence of polarization with the results obtained for BFO films grown by PLD and sputtering.⁸ These three films prepared by different growth methods showed very similar behavior. In all the cases, switched polarization values of $\sim 120 \mu\text{C}/\text{cm}^2$ were observed, which began to saturate at 400–450 kV/cm. Moreover, the polarization showed weak pulse width dependence in the range of 1 μs –1 ms, as shown in Fig. 3(d). This demonstrates that the measured polarization switching is an intrinsic property of BFO films, and is not dominated by leakage, which was a critical obstacle in determining the ferroelectric property of bulk BFO.¹¹

BFO films were also grown on (001) Si using a 20 nm-thick STO layer as a template, and their properties were compared with those of films grown on STO substrates. Figure 4 shows P - E loops of BFO films grown on such substrates. Polarization values (ΔP) of 85–90 $\mu\text{C}/\text{cm}^2$ and co-

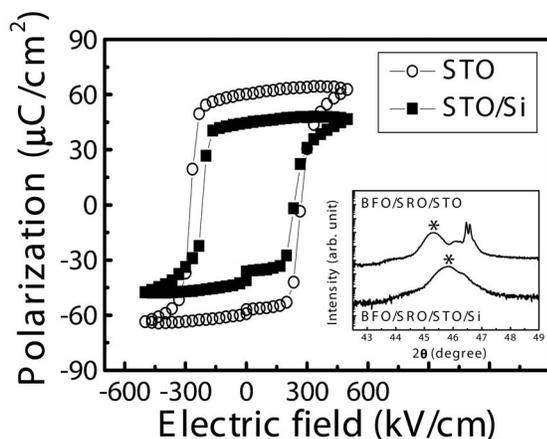


FIG. 4. P - E hysteresis loops obtained from BiFeO_3 films on $\text{SrRuO}_3/\text{SrTiO}_3$ and $\text{SrRuO}_3/\text{SrTiO}_3/\text{Si}$ substrates. X-ray diffraction patterns around (002) BiFeO_3 peaks are shown in the inset.

ercive fields of $\sim 225 \text{ kV}/\text{cm}$ were measured for BFO films grown on Si substrate. These values are smaller than those obtained for BFO films grown on STO, due to the in-plane tensile stress induced by large thermal mismatch with silicon.⁴ Out-of-plane lattice constants of 4 and 3.96 \AA were observed for BFO films (200 nm) grown on STO and Si substrates, respectively.

In summary, we have demonstrated a viable chemical vapor deposition process, which enables the growth of high quality BiFeO_3 thin films. The implementation of such a process into the potential FeRAM technology requires the solution for some key issues. First, the leakage current must be lowered by at least an order of magnitude. This requires a careful study of the defect chemistry of the films as a function of Bi-Fe ratio as well as other process parameters such as the substrate temperature and oxygen ambient during cooling. Second, the coercive field must be reduced to $\sim 50 \text{ kV}/\text{cm}$ (e.g., 1 V for a 200 nm-thick film). Careful studies of the switching mechanisms in these films (180° vs $71/109^\circ$ switching, and the interplay between ferroelectric and ferroelastic switching)^{8,12} are needed. Third, the growth temperature must be reduced. Preliminary studies indicate that this should be possible, in agreement with the reports of Yun *et al.*¹³ From the CVD chemistry point of view, it is critical to explore the processing space to identify the possibility of a “self-regulating” reaction zone. In this regard, our preliminary results show that a postdeposition oxygen flush of the film surface appear to hold promise in terms of removing the excess Bi on the surface.

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