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Ferroelectric characteristics of $BiFeO_3$ thin films prepared via a simple chemical solution deposition

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$BiFeO_3$ (BFO) thin films were fabricated on $Pt(111)/Ti/SiO_2/Si$ substrates by using a polymeric precursor solution under appropriate crystallization conditions. The capacitance dependence on voltage is strongly nonlinear, confirming the ferroelectric properties of the films resulting from the domain switching. The leakage current density increases with annealing temperature. The polarization electric field curves could be obtained in BFO films annealed at 500 °C, free of secondary phases. X-ray photoelectron spectroscopy spectra of films annealed at 500 °C indicated that the oxidation state of Fe was purely 3+, demonstrating that our films possess stable chemical configurations. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2715513]

I. INTRODUCTION

Multiferroic materials are becoming shining stars on the stage of new materials, which have attracted ever-increasing interest from perspectives of both fundamental physics and practical applications.[1] To date more than 80 single-phase multiferroic compounds have been grown either as a discrete composition or as a solid solution. Among these, $BiFeO_3$ is a compound most extensively studied, which is ferroelectric, ferroelastic, and weakly ferromagnetic.[2,3] $BiFeO_3$ (BFO) is characterized by a rhombohedrally distorted perovskite structure having unit cell parameters $a_r = 3.96$ Å and $\alpha_r = 0.6°$.[4,5] The high polarization and piezoelectric response in thin $BiFeO_3$ films suggests a possible environmentally benign substitute for Pb-based ferroelectrics, though considerable optimization of ferroelectric properties is necessary.[6] Interest in this compound is due to its high Curie temperature ($T_C \sim 1100$ K) and magnetic ordering temperature ($T_N \sim 650$ K) [3,7] which are important for practical applications. However, ferroelectric characterization on bulk $BiFeO_3$ has been very difficult because of its low resistivity, which is likely due to defects and nonstoichiometry.

Recently, a few studies focusing on the preparation of $BiFeO_3$ thin films have presented a promising potential for this material. Among them, Palkar *et al.*[8] first observed ferroelectric hysteresis loop of $BiFeO_3$ films prepared by pulsed laser deposition (PLD) with a saturation polarization $P_s = 2.2$ $\mu C/cm^2$ at room temperature. Wang *et al.*[9] reported PLD epitaxial $BiFeO_3$ thin films with a greatly enhanced polarization with remanent polarization $P_r = 55$ $\mu C/cm^2$ along (001). Yun *et al.*[10,11] reported $P_r = 35.7$ $\mu C/cm^2$ for PLD polycrystalline $BiFeO_3$ thin films, and in their subsequent work, they have obtained a giant $P_s = 158$ $\mu C/cm^2$ at 90 K. In these works the PLD technique was employed and most $BiFeO_3$ films were grown on the oxide electrodes[9] which are difficult to synthesize in comparison with the metal electrodes sputtered on Si substrates.

The major problem of BFO thin films is their low electrical resistivity, which affects the application of their ferroelectric order at room temperature. The relatively high conductivity of BFO films is known to be attributed to the variable oxidation states of Fe ions (Fe^{3+} to Fe^{2+})[12] which requires oxygen vacancies for charge compensation and produces electron hopping in films. The oxidation state of Fe is greatly dependent on the processing conditions and the type and amount of dopants.

In previous works, our group had reported the preparation of thin films by the polymeric precursor method.[13] The overall process consists of preparing a coating solution based on metallic citrate polymerization. The precursor film is deposited by dip or spin coating and then treated to eliminate the organic material and synthesize the desired phase. In this work, we use a simple chemical solution spin-coating technique to prepare pure-phase $BiFeO_3$ thin films on a common $Pt(111)/Ti/SiO_2/Si$ substrate. We report the growth and ferroelectric properties of polycrystalline BFO thin films prepared by chemical solution deposition under various crystallization conditions.

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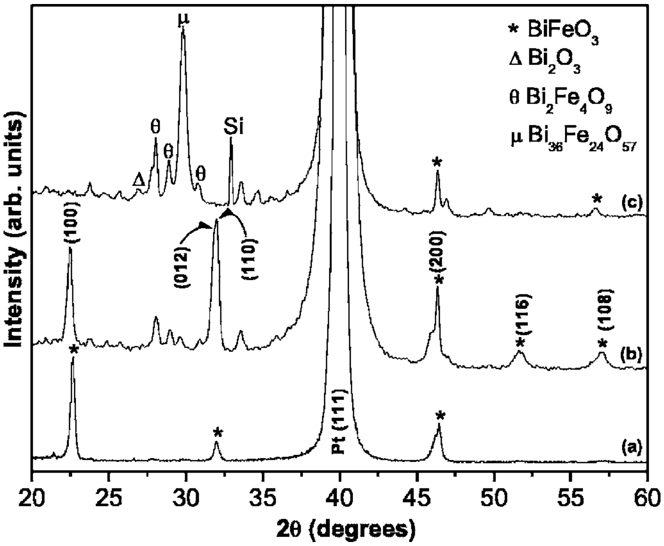

FIG. 1. X-ray diffraction diagram of BFO films annealed in static air for 2 h at (a) 500, (b) 600, and (c) 700 °C.

II. EXPERIMENT

Iron (III) nitrate nonahydrate $[Fe(NO_3)_3 \cdot 9H_2O]$, 99.5% purity (Merck) and bismuth nitrate (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. 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 a $Pt(111)/Ti/SiO_2/Si$ substrate. The BFO films were completely crystallized after annealing for 2 h at temperatures ranging from 500 to 700 °C. Multilayered films were obtained by spinning ten times the deposition solution on the surface of the substrate at 5000 rpm.

In this work, an excess of 5 wt % Bi was added to the solution, aiming to minimize the bismuth loss during the thermal treatment. Without this additional bismuth the pure phase could not be obtained. Phase analysis was performed at room temperature by x-ray diffraction in the $\theta - 2\theta$ mode scan, recorded on a Rigaku diffractometer (Rigaku-DMax 2500PC) using Cu $K\alpha$ radiation. The thickness of the annealed films was studied 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. The surface roughness was examined by atomic force microscopy 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 present oxygen vacancies.

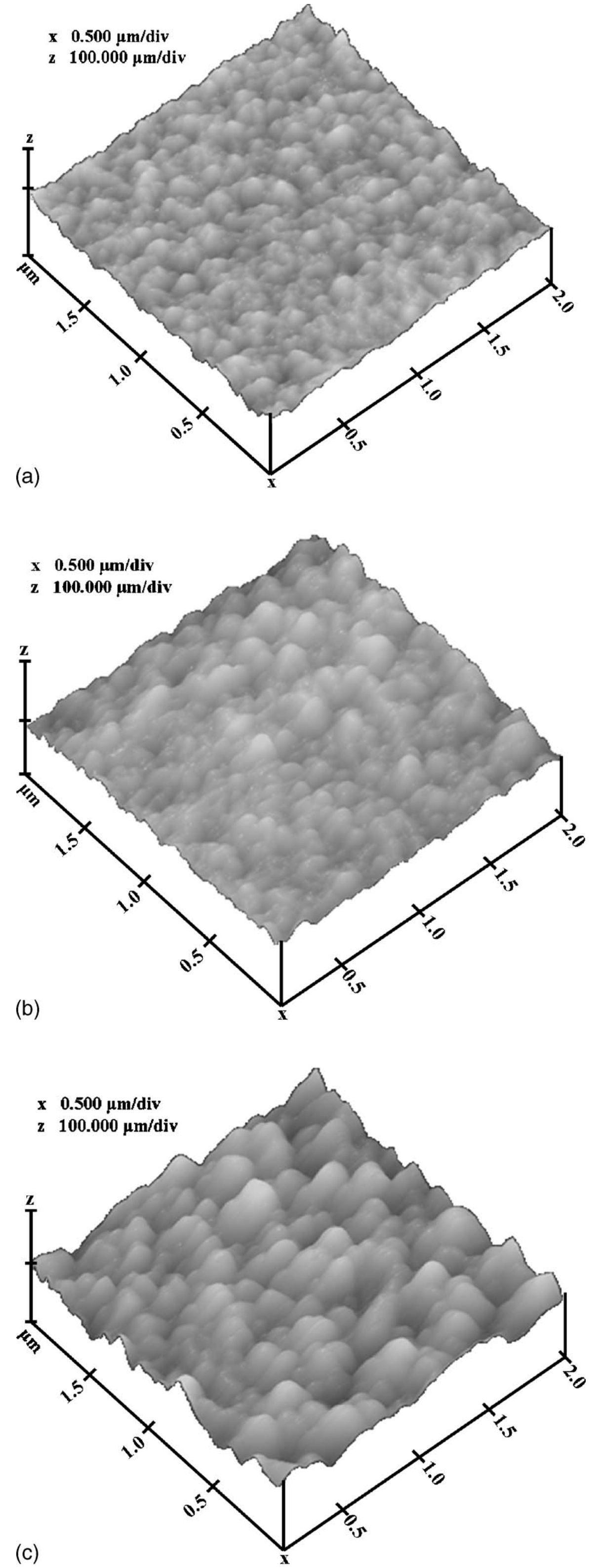

FIG. 2. AFM images of BFO films annealed in static air for 2 h at (a) 500, (b) 600, and (c) 700 °C.

The capacitance-voltage characteristics were measured in the metal-ferroelectric-metal configuration using a small alternating current (ac) signal of 10 mV at 100 kHz. The ac signal was applied across the sample, while the direct current (dc) was swept from positive to negative bias. A PHI-5702 multifunction x-ray photoelectron spectrometer was used, working with an Al $K\alpha$ x-ray source of 29.35 eV passing

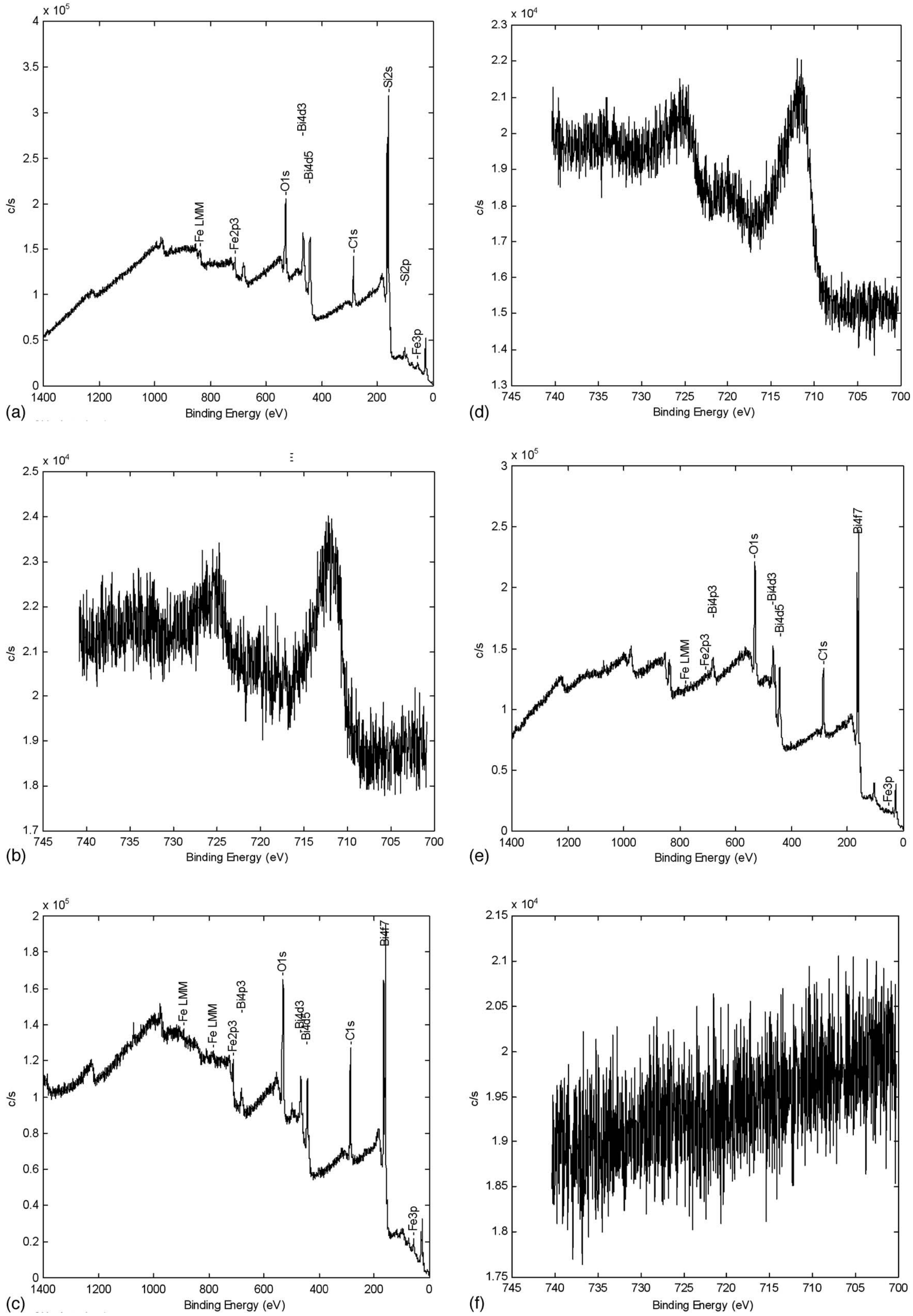

FIG. 3. XPS spectra of (a) Bi 4f, (b) Bi 5d, (c) Fe 2p, (d) O 1s peaks for BFO thin films annealed in static air for 2 h at (a) and (b) 500, (c) and (d) 600, and (e) and (f) 700 °C.

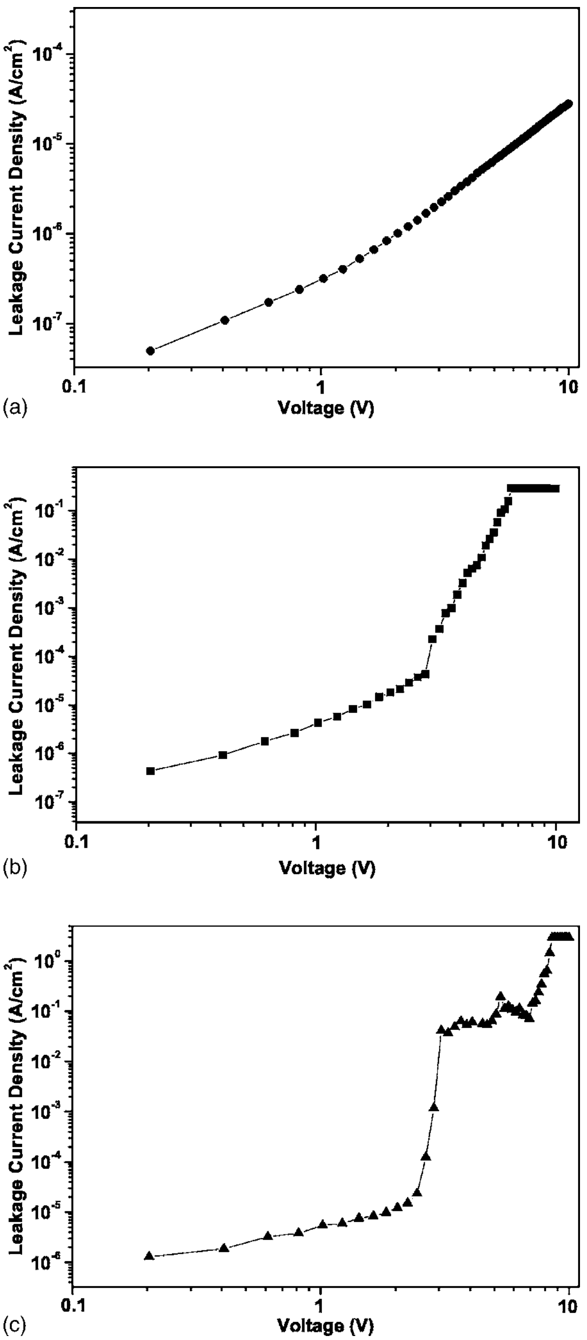

FIG. 4. Leakage current density of BFO films annealed in static air for 2 h at (a) 500, (b) 600, and (c) 700 °C.

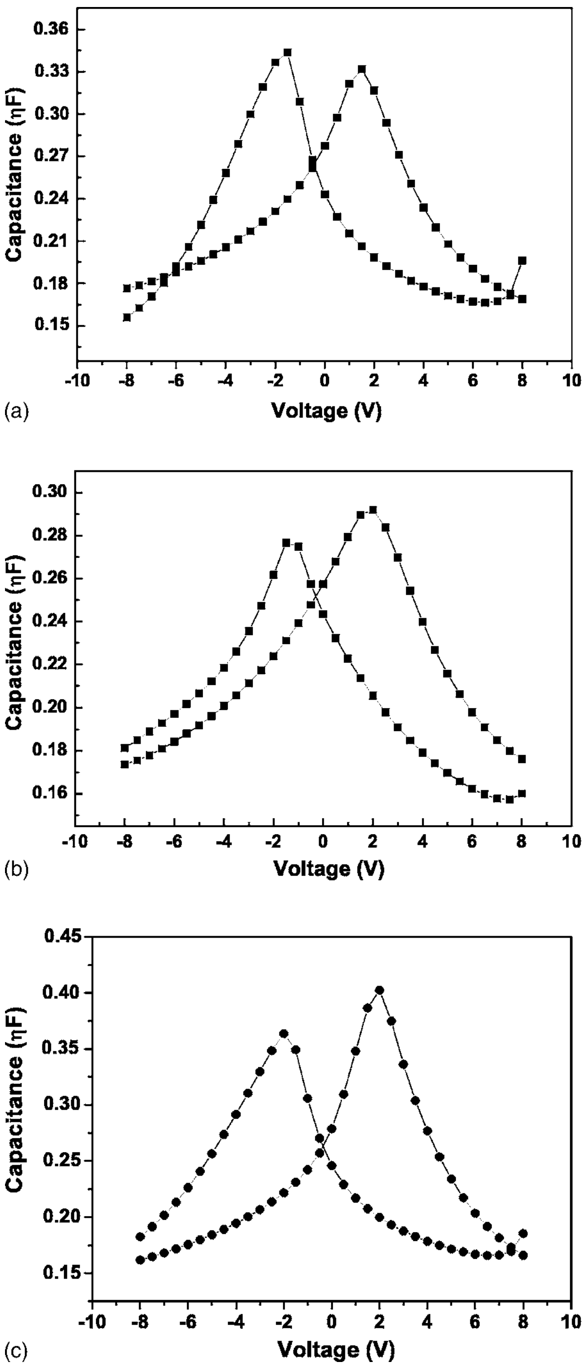

FIG. 5. Capacitance-voltage curves of BFO films annealed in static air for 2 h at (a) 500, (b) 600, and (c) 700 °C.

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 1*s* line, which appears in the photoelectron spectra of the as-received samples. The ferroelectricity was investigated using a Sawyer–Tower circuit attached to a computer-controlled standardized ferroelectric test system (Radiant Technology 6000 A).

III. RESULTS AND DISCUSSION

Figure 1 displayed the x-ray diffraction (XRD) patterns of BFO films annealed at various temperatures, demonstrating that a pure perovskite phase is formed at 500 °C with no second phases detected. This means that the amount of second phases was less than 1 vol. %, which was approximately the detection limit of the XRD system used. The diffraction peaks were identified using the pseudocubic structure. The intensity of (100) and (200) diffraction peaks were strong with respect to that of the (110) peak. As the temperature increases, secondary phases, such as Bi_2O_3, $Bi_2Fe_4O_9$, and $Bi_{36}Fe_{42}O_{57}$ were present in the BFO films. Also, other unidentified phases were present, especially in the film annealed at 700 °C for 2 h.

Atomic force microscopy (AFM) images of BFO thin films annealed at 500, 600, and 700 °C for 2 h are illustrated in Fig. 2. The BFO films were dense with uniform grains for films annealed at 500 °C without the presence of any second

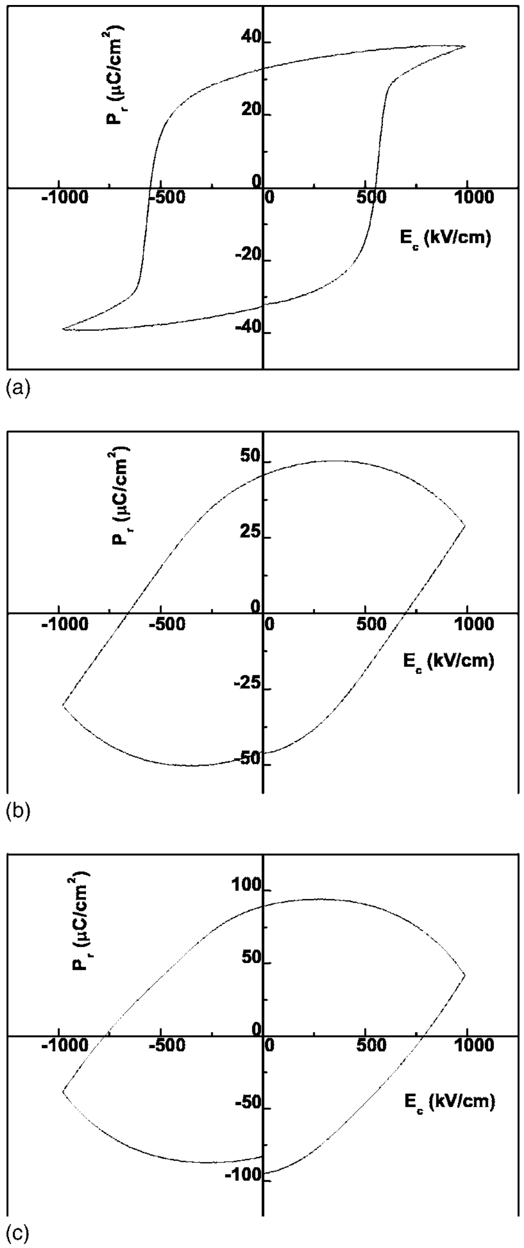

FIG. 6. Hysteresis loops of BFO films annealed in static air for 2 h at (a) 500, (b) 600, and (c) 700 °C.

phase [Fig. 2(a)]. The grains started to grow abnormally at 600 °C, when some grains grew faster than others and tended to consume surrounding small grains [Fig. 2(b)]. The size of the large grain of BFO thin film annealed at 600 °C was about 170 nm, while that of the small ones varied from 90 to 120 nm. The grain size and the uniformity of the microstructure were thought to have great influence on the leakage properties.

Generally, it was assumed that the conduction mechanism of BFO was related to the hopping of electrons from Fe^{2+} to Fe^{3+} when oxygen vacancies are present in the lattice, which act as a "bridge" between Fe^{2+} and Fe^{3+} and play an important role in the electronic conduction.[14] In order to identify the chemical bonding of BFO thin films, we performed x-ray photoelectron spectroscopy (XPS) studies. The wide-range spectrum of BFO thin films deposited at several temperatures is shown in [Figs. 3(a), 3(c), and 3(e)]. The spectrum expanded from 700 to 745 eV is also shown. The 3/2 and 1/2 spin-orbit doublet components of the Fe $2p$ photoemission were located at 711.1 and 724.6 eV, respectively. The XPS results show that BFO thin film annealed at 500 °C has a single phase with a Fe^{3+} valence state, consistent with XRD result shown in Fig. 1. The 3/2 and 1/2 spin-orbit doublet of the Fe $2p$ photoemission located at 711.1 and 724.6 eV were identified as Fe^{3+}, respectively. No Fe^{2+} and Fe were found. The oxidation state of Fe was purely 3+, which was advantageous for producing BFO films with low leakage [Fig. 3(b)]. The absence of Fe^{2+} ions suggests the reduction of oxygen vacancies in our films, which may be one of the reasons for enhanced ferroelectric property, as will be discussed in the present article. Although the film annealed at 600 °C has a small amount of secondary phases, the Fe^{2+} and Fe^{3+} ions are not seen in the spectrum because of their presence being below the XPS detection limit or their photoemission coinciding in binding energies with the other two peaks [Fig. 3(d)]. No evidence of Fe $2p$ photoemission is noted in the film annealed at 700 °C [Fig. 3(f)]. This is a surprising result and indicates that the penetration depth of only a few nanometers of XPS technique was not enough to exclude the possible difference between the topmost surface and inside bulk of the film. New experiments are being performed in order to probe these differences.

Figure 4 plotted the current density versus electric field curves of BFO films annealed at various temperatures. Generally, the leakage current density should be less than 10^{-7} A/cm^2 during operation in memory device applications. The leakage current density of the film annealed at 500 °C is around 10^{-7} A/cm^2 demonstrating the quality of the obtained BFO films [Fig. 4(a)]. The leakage current for the films annealed at 600 and 700 °C was only 10^{-6}A/cm^2 at 1 V, which is much lower than those reported in the literature [Figs. 4(b) and 4(c)]. They were 10^{-5} A/cm^2 chemical solution deposition (CSD)[15] and 5×10^{-1} A/cm^2 (PLD)[16] for pure BFO films. The leakage current increases with annealing temperature and its dependence is addressed to the presence of secondary phases. Increase temperature leads to bigger grains and also to raise of leakage current once the grain growth became nonuniform. The strong dependence of leakage current on grain size suggested that grain boundary related mechanisms dominated the conduction.

Figure 5 illustrates the capacitance-voltage curves for BFO films obtained at 100 kHz and dc sweep voltage from +8 to −8 V. The capacitance of the film showed a strong dependence on the applied voltage, confirming the ferroelectric properties of the film resulting from the domain switching. There is no polarization gap toward along the positive and negative direction of the applied electric field for the film annealed at 500 °C for 2 h also indicating symmetry in the vicinity of the spontaneous polarization switching [Fig. 5(a)]. On the other hand, the films annealed at higher temperatures (600 and 700 °C) present a polarization gap toward the direction of negative field, suggesting the presence of charge carriers trapped near the electrode/film interface [Figs. 5(b) and 5(c)]. Typically, this behavior is mainly attributed to the difference of work function, crystallographic defect distribution, and thermal history between top electrode and bottom electrode.

The room temperature $P-E$ hysteresis loops of BFO thin films annealed at several temperatures are shown in Fig. 6. The BFO films annealed at 600 and 700 °C for 2 h exhibit poor $P-E$ hysteresis loops, which has been typically observed from conductive ferroelectrics [Figs. 6(b) and 6(c)]. In contrast, the BFO thin film annealed at 500 °C shows well-saturated hysteresis characteristics with a remanent polarization (P_r) of 31 $\mu C/cm^2$ and a coercive field (E_c) of 560 kV/cm at a maximum applied electric field of 1000 kV/cm [Fig. 6(a)]. We attribute the value of our P_r to the intense (100) preferred orientation. According to Wang *et al.*,[12] the ferroelectricity of BFO originates from the relative displacements of Bi ion and Fe-O octahedron along the (111) orientation in epitaxial BFO films and the projection polarization along the (110) orientation is larger than that of the (100) orientation. Since the films in our work are intense (100) we reasonably did not expect a larger polarization. A high coercive field was observed in our BFO films, which is probably originated from the small grain size of the BFO films. The polarization switching is usually more difficult in films with fine grains. Therefore, to increase the grain size and reduces the coercitive field, the use of oxygen atmosphere and substitution of bismuth site are under progress, and the results will be published in the near future.

IV. CONCLUSIONS

Single phase BFO thin films were deposited at 500 °C for 2 h on the $Pt(111)/Ti/SiO_2/Si$ substrates by the chemical solution deposition method. The leakage-current density of the film annealed at low temperature was around 10^{-7} A/cm^2 with a remanent polarization P_r of 31 $\mu C/cm^2$ at room temperature. These results indicate that the control of BFO film composition is effective to reach good ferroelectric properties. Furthermore, it was clearly demonstrated that the good ferroelectric BFO thin films could be fabricated by a chemical solution deposition method at low temperatures, which is advantageous for real device applications.

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