Epitaxial BiFeO3 Thin Films Fabricated by Chemical Solution Deposition

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Epitaxial $BiFeO_3$ thin films fabricated by chemical solution deposition

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Epitaxial $BiFeO_3$ (BFO) thin films were fabricated on (001)-, (110)-, and (111)-oriented single-crystal $SrRuO_3$(SRO)/$SrTiO_3$(STO) structures by chemical solution deposition. X-ray diffraction indicates the formation of an epitaxial single-phase perovskite structure and pole figure measurement confirms the cube-on-cube epitaxial relationship of BFO‖SRO‖STO. Chemical-solution-deposited BFO films have a rhombohedral structure with lattice parameter of 0.395 nm, which is the same structure as that of a bulk single crystal. The remanent polarization of approximately 50 $\mu C/cm^2$ was observed in BFO (001) thin films at 80 K. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2196477]

Multiferroic materials are important for realizing multifunctional devices used in information storage, spintronics, and so on. Strong coupling between ferroelectric and antiferromagnetic or ferromagnetic domain walls has been reported in rare-earth manganites[1–3] at low temperatures. Multiferroic $BiFeO_3$ (BFO) is a suitable candidate to attain the ferroelectric and antiferromagnetic domain coupling at room temperature (RT), due to its high Curie temperature (T_c) (around 850 °C)[4,5] and Neel temperature (T_N) (around 370 °C).[6] The lattice structure of a BFO bulk single crystal is a rhombohedrally distorted perovskite, which belongs to the space group R3c (or C_6^{3V}) with unit-cell parameters $a=0.396$ nm and $\alpha=89.4°$.[7] Large polarizations are expected in BFO due to the large distortion of the lattice and high Curie temperature. However, polarizations actually measured in a bulk single crystal were only 3.5 $\mu C/cm^2$ and 6.1 $\mu C/cm^2$ along the (001) and (111) axes, respectively.[8]

Recently, enhanced ferroelectric properties have been reported in BFO thin films fabricated by pulsed laser deposition (PLD)[9–11] and chemical solution deposition,[12] although it is difficult to measure electrical properties at RT because of their low resistivity. The large remanent polarization in BFO thin films was initially thought to be a stress-induced property,[10] but more recently it is interpreted to be an intrinsic property which even appears in unstressed films.[13] Along with a deep consideration of the enhanced polarization mechanism, new applications, such as the formation of BFO nanotubes, have been started.[14]

Epitiaxial BFO films grown by PLD on (111)-oriented $SrRuO_3/SrTiO_3$ (SRO/STO) structures have a rhombohedral structure, which is the same as that of single crystals, but films grown on (110)- or (001)-oriented SRO/STO structures are monoclinic.[10] It has also been determined from synchrotron x-ray diffraction (XRD) analysis that the lattice of the (001)-oriented film has a low-symmetry phase close to the M_A-type monoclinic structure.[15] However, BFO films grown by liquid phase epitaxy on (001)-oriented SRO/STO have a rhombohedral structure.[16] These results indicate that the deposition process plays an important role in determining the crystal structure of BFO thin films. In this work, we prepare epitaxial BFO thin films using chemical solution deposition (CSD) and characterize the crystal structure and electrical properties of the films. CSD is particularly important from an industrial aspect because of its suitability for large-area deposition and for exact stoichiometry composition control.

In the experiment, SRO bottom electrodes were first formed on STO substrates using radio-frequency sputtering. A typical film thickness is 100 nm. It was found from XRD analysis that the SRO films grew epitaxially on the substrates. Then, BFO thin films were formed by depositing sol-gel chemical solution on SRO(001)/STO(001), SRO(110)/STO(110), and SRO(111)/STO(111) structures. Stoichiometric solution of BFO with a concentration of 0.2 mol/l (Toshima Mfg. Co., Ltd.) was spin-coated at 3000 rpm for 30 s, dried at 240 °C for 3 min, and pre-fired at 350 °C for 10 min in air. This process was repeated several times to obtain the desired thickness of the films, and then the films were annealed at 600 °C for 15 min in a nitrogen atmosphere. Electron-beam evaporation was used for depositing Pt top electrodes of 3.14×10^{-4} cm^2 and 0.79×10^{-4} cm^2 in areas through a shadow mask. The crystal structures of the films were investigated by high-resolution XRD with a four-axis diffractometer (X'Pert-Pro MPD, Philips). The electrical properties of the film capacitors were measured using a standardized ferroelectric test system (Toyo Corp. FCE) and an HP4156A precision semiconductor parameter analyzer (Hewlett-Packard).

Figure 1 shows XRD θ-2θ scan of BFO films grown directly on STO (001) and on sputtered SRO films on (001)-, (110)-, and (111)-oriented STO substrates. All BFO films show only the (00 *l*), (110), and (111) peaks corresponding to the substrates without any secondary phase, which demonstrates that the BFO films are well (001), (110), and (111) oriented along the normal to the substrate. In the BFO film directly grown on STO, the out-of-plane lattice parameter of 0.395 nm was observed. In the BFO film on SRO(001)/STO(001), we could distinguish (002) peaks of BFO, SRO and STO, because the out-of-plane lattice parameter of SRO grown by sputtering was 0.399 nm in pseudocubic symmetry, as we have repoted earlier.[17] The in-plane epitaxial relationships between the films and the substrates were established by the pole figure measurement at a fixed 2θ angle corresponding to the BFO (110) diffraction, as shown in the insets of Fig. 1. They confirm the cube-on-cube epitaxial relationship as follows: BFO(001)‖SRO(001)‖STO(001),

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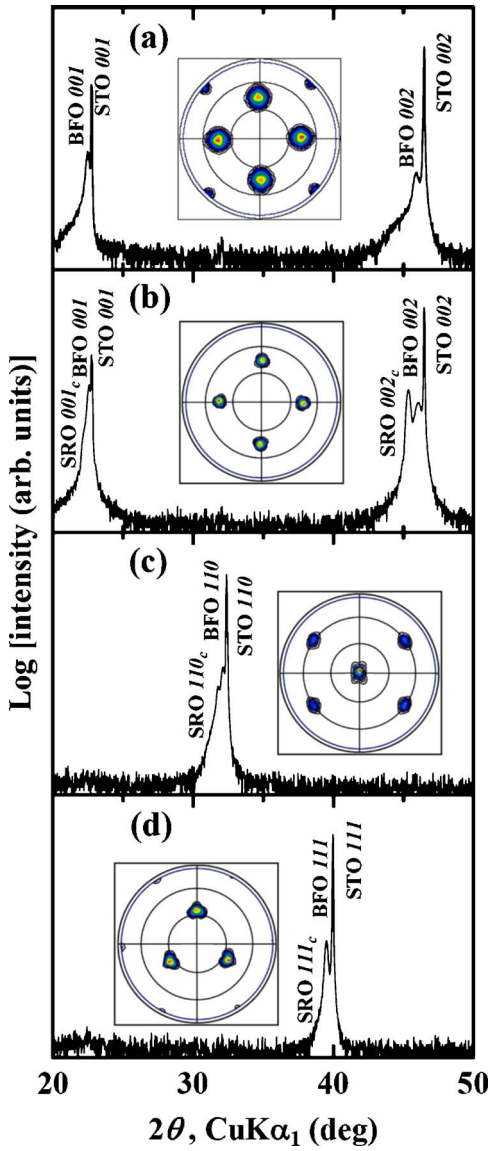

FIG. 1. (Color online) θ-2θ x-ray diffraction patterns and pole figures (inset) of BFO films deposited on (a) (001)-oriented STO and SRO-coated STO with (b) (001), (c) (110), and (d) (111) orientations.

BFO(110)‖SRO(110)‖STO(110), and BFO(111)‖SRO(111)‖STO(111). To the best of our knowledge, this is the first demonstration of epitaxial growth of BFO films by CSD.

In order to estimate more detailed information on crystal structure, we measured the two-dimensional reciprocal space mapping. Figure 2 shows the results of reciprocal space mappings near BFO (004) and (204) diffraction spots of BFO films grown on SRO(001)/STO(001). The vertical axis is set parallel to STO[001] and horizontal axis is set parallel to STO[100], respectively. The results show that BFO (004) and (204) diffraction spots are widely spread compared with those of STO and SRO. The broad distribution of x-ray intensity can be understood as a low crystalline quality of the BFO epatixial film grown by CSD. It can be derived from these figures that BFO films have a rhombohedrally distorted perovskite unit cell with $a_{\parallel} \approx 0.394$ nm, $a_{\perp} \approx 0.395$ nm, and $\beta \approx 89.1°$.

To characterize the electrical properties of the films, we measured current versus voltage (I-V) and polarization versus electric field (P-E) characteristics of a Pt/BFO(001)/SRO(001)/STO(001) capacitor structure. Figure 3 shows

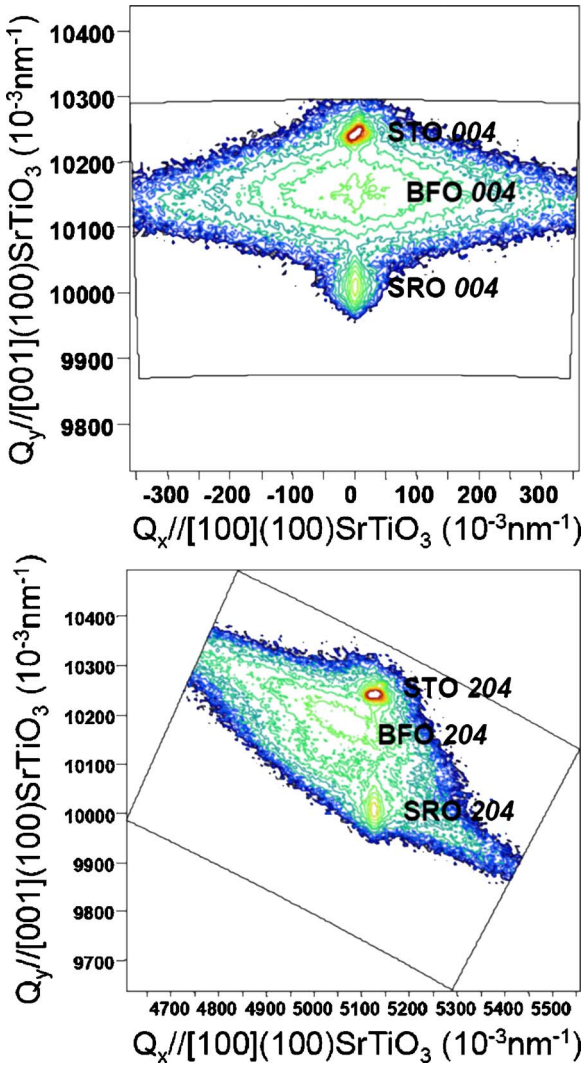

FIG. 2. (Color online) XRD reciprocal space mappings around BFO (004) and (204) diffraction spots of a BFO film grown on SRO(001)/STO(001) structure.

I-V characteristics of the capacitors annealed for 15 min at 600 °C in N_2 atmosphere and measured at RT as well as at 80 K. As shown in Fig. 3, the leakage current density in the BFO film is as high as 8 A/cm^2 at RT with an applied electric field of 0.5 MV/cm, and it dramatically decreases to

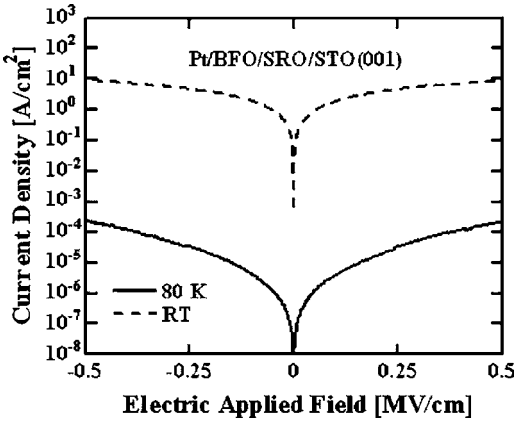

FIG. 3. I-V characteristics of Pt/BFO/SRO/STO(001) film capacitors annealed for 15 min at 600 °C in a N_2 atmosphere and measured at RT and 80 K.

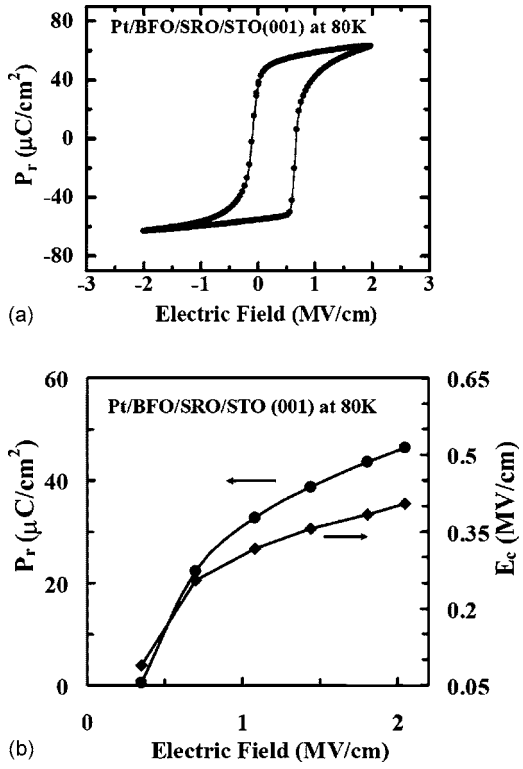

FIG. 4. (a) *P-E* hysteresis loops of Pt/BFO/SRO/STO(001) film capacitor measured at 80 K and (b) variation of polarization and coercive field with applied electric field.

2×10^{-4} A/cm^2 at 80 K. Because of the reduced leakage current, we could measure the polarization in BFO films at 80 K. Figure 4 shows a *P-E* hysteresis loop. As shown in Fig. 4, the hysteresis loop shifts to the positive direction, which is considered to be due to the asymmetric electrode materials. The coercive field of the BFO film was around 0.3 MV/cm. At 80 K, remanent polarizations were obtained for electric fields higher than 0.3 MV/cm, and they were well saturated for electrical fields higher than 1.5 MV/cm. Remanent polarization of approximately 50 μC/cm^2 was obtained in an epitaxial (001)-oriented BFO film at 2 MV/cm. This value is closed to the reported remanent polarization in pulsed laser deposited BFO films on a (001)-oriented SRO/STO structure[9] and approximately one-half of the value on a (111)-oriented structure.[10]

In summary, epitaxial BFO thin films were successfully deposited on SRO-coated (001)-, (110)-, and (111)-oriented STO substrates by CSD. BFO films show only (00 *l*), (110), and (111) diffraction peaks on respective (001), (110), and (111) substrates without any secondary phase. The in-plane epitaxial relationships between the films and the substrates were confirmed to be the cube-on-cube epitaxial relationship of BFO$\|$SRO$\|$STO. (001)-oriented BFO films grown by CSD were found to have a rhombohedrally distorted perovskite unit cell with $a_{\|}\approx0.394$ nm, $a_{\perp}\approx0.395$ nm, and $\beta\approx89.1°$. The leakage current density of the BFO films was decreased to 2×10^{-4} A/cm^2 at 80 K with applied electric field of 0.5 MV/cm, and because of the improved leakage current characteristic, we could measure the electrical properties of the BFO films. The remanent polarization of approximately 50 μC/cm^2 was obtained in epitaxial (001)-oriented BFO thin films.

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