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Electrical and piezoelectric properties of BiFeO$_3$ thin films grown on Sr$_x$Ca$_{1-x}$RuO$_3$-buffered SrTiO$_3$ substrates

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INTRODUCTION

Bismuth ferrite (BiFeO$_3$) has been extensively studied due to its unique multiferroic properties, which are promising for applications in novel magnetoelectric (ME) devices. Furthermore, promising photovoltaic performances, such as large open-circuit voltage, high quantum efficiency, and appreciable response to visible lights, have been observed. Domain walls and interfaces (grain boundaries and ferroelectric-electrode interfaces) are found to play important roles in the photovoltaic effects. BiFeO$_3$ is ferroelectric (FE) and antiferromagnetic (Anti-FM) in bulk samples, whereas it is FE and ferromagnetic (FM) in thin films and nanoparticles. Moreover, the FE Curie temperature and Anti-FM Neel temperature of BFO are 810°C and 380°C, respectively, which are high enough for normal applications.

The appearance of FM behavior in BFO thin films is related to residual strain, which deforms the crystallographic structure from rhombohedral to tetragonal to some extent. Such deformation suppresses the Anti-FM spiral spin structure and results in the appearance of FM (Ref. 11) and leads to a large electrical remnant polarization (~130 µC/cm$^2$). Recently, a substantial piezoelectric response (~5%) was observed in BFO films with coexistence of tetragonal and rhombohedral crystal structures. Additionally, transitions between the tetragonal phase and the rhombohedral phase can be controlled by external electrical field and a new temperature-induced phase transitions around 100°C was recently observed in these highly strained BFO films. It seems clear, then that strain considerably affects the magnetic, electrical and piezoelectric behaviors of BFO films. Here, we report on how the introduction of different strain states affects BFO thin films grown on different substrates. To this end, we chose Sr$_x$Ca$_{1-x}$RuO$_3$ (SCRO; x = 1, 0.67, 0.33, 0) buffered SrTiO$_3$ (001) crystals as the substrates. SCRO is highly conductive and is often used as the bottom electrode in electrical characterizations. The lattice constants of pseudo-cubic SCRO are 3.92 Å, 3.89 Å, 3.87 Å, and 3.84 Å, for x = 1, 0.67, 0.33, and 0, respectively (as shown below). The lattice constant of bulk BFO is 3.96 Å, which is clearly larger than that of SCRO. Therefore, the expected lattice mismatch would be 1.1%, 1.9%, 2.3%, and 3.0%, respectively. In addition, the expected stress state would be compressive. Although previous work used thin SrRuO$_3$-buffered layers (10–80 nm thick) as the bottom electrode in BFO films and varied the strain state by using different substrates, such as SrTiO$_3$, LaAlO$_3$, YAlO$_3$, and Pt, the effects of conductive buffer layers on the performance of BFO thin films has not yet been studied systematically.

EXPERIMENTAL

SCRO and BFO targets were synthesized using the conventional solid-state reaction technique. BiFeO$_3$ ceramics were prepared from reagent-grade Bi$_2$O$_3$ and Fe$_2$O$_3$ powders (Sigma-Aldrich). The raw materials were well mixed by ball-milling, pressed into 1-in.-diameter disks under a uniaxial pressure of 200 MPa, and then sintered at 795°C for 30 min. Excess Bi was added to compensate for the loss of Bi during processing. The Sr$_x$Ca$_{1-x}$RuO$_3$ targets were prepared using SrCO$_3$, CaCO$_3$, and RuO$_2$ raw powders, which were sintered at 1500°C for 4 h. The target composition and crystal structure were confirmed by x-ray fluorescence (XRF) and x-ray diffraction (XRD) patterns.

The SCRO-buffer layers and BFO films were successively deposited onto SrTiO$_3$ (001) single-crystal substrates using pulsed laser deposition (PLD). During deposition, the substrate temperature was fixed at 750°C for SCRO and 650°C for BFO, and the oxygen pressure was kept at 150 mTorr for both layers. The thicknesses of the SCRO layers and BFO layers were both around 380 nm. The laser (KrF, 248 nm) was operated at 5 Hz with an energy density of 7 J/cm$^2$ at the target surface. The distance between the target and substrate was 4 cm. After deposition, 400 Torr of oxygen was
introduced into the chamber and the sample was annealed at 650 °C for 20 min under this oxygen environment. Au electrodes of that were 20 nm thick and 0.2 mm in diameter were sputtered onto the BFO films. The crystal structure of the samples was characterized by an x-ray diffractometer (XRD, Bruker D8 Discover). The surface morphology and piezoelectric response were characterized by atomic force microscopy (AFM, Agilent 5400). Electrical leakage currents and ferroelectric polarization were measured using a ferroelectric tester (aixACCT).

RESULTS AND DISCUSSION

The XRD patterns of the BFO thin films and the SCRO-buffer layers are shown in Figure 1. The SCRO-buffer layers were well crystallized and oriented in the (001) direction. The BFO films grown on SrRuO3- and Sr0.67Ca0.33RuO3-buffered substrates exhibited only (001) orientations. In the BFO films grown on Sr0.33Ca0.67RuO3- and CaRuO3-buffered substrates, a weak (110) peak, around 10% of the intensity of the major (001) peak, also appeared, as shown in Figure 1(a). The larger lattice mismatch between the BFO films and these two buffered layers is the likely reason for this difference. In all the films, tiny amounts of secondary-phase Bi25FeO40 and Bi2Fe4O9 were detected. Decomposition of the BFO film during high-temperature processing could be the origin of the phase impurities.22–24 Enlarged views of the (001) peaks are shown in Figures 1(c) and 1(d) for BFO films and the buffer layers, respectively. The (001) diffraction positions (2θ) of the buffer layers were 22.51°, 22.58°, 22.63°, and 23.12°, for SrRuO3, Sr0.67Ca0.33RuO3, Sr0.33Ca0.67RuO3, and CaRuO3, respectively. The corresponding bulk values were 22.68°, 22.86°, 22.96°, and 23.13°, as shown in the inset of Figure 1(d). Low shifts of XRD peak positions (or increase of lattice constant) were present in all buffer layers, indicating tensile stress in the SCRO layers. In the BFO films, the (001) peak positions were 22.42°, 22.44°, 22.48°, and 22.50°, for buffer layers of SrRuO3, Sr0.67Ca0.33RuO3, Sr0.33Ca0.67RuO3, and CaRuO3, respectively. Meanwhile, the BFO target had its (001) peak at 22.40°. In comparison with its bulk value, the lattice constant of BFO film decreased gradually with different SCRO buffer layers from SrRuO3 to CaRuO3. Therefore, the stress state (compressive) of the BFO films increased gradually as the buffer layer changed from SrRuO3 to CaRuO3.

AFM images showing the surface microstructures of the BFO films are presented in Figure 2. All the samples are dense, uniform with no large pores. The grain sizes were...
260 nm, 207 nm, 186 nm, and 134 nm in films with SrRuO$_3$, Sr$_{0.67}$Ca$_{0.33}$RuO$_3$, Sr$_{0.33}$Ca$_{0.67}$RuO$_3$, and CaRuO$_3$-buffer layers, respectively. The corresponding surface roughness ($R_a$) values were 15.8 nm, 14.6 nm, 12.1 nm, and 7.0 nm, respectively. The BFO film grown on the SrRuO$_3$-buffered layer had the largest grain size and also the most rough surface, while the smallest grain size and the smoothest surface were found in the film with the CaRuO$_3$-buffer layer. The smaller grains, or more grain boundaries, observed in the BFO on the CaRuO$_3$-buffer layer can be understood in terms of film energy. In largely strained and thick films (thicker than tens of nanometers), grain boundaries are energetically favorable to reduce the strain energy. This will result in smaller grains. Another possible reason for the difference in BFO grain sizes may be associated with the microstructures of the underlying buffered layers, which are shown in Figure 3. The roughness values ($R_a$) were 1.79 nm, 0.52 nm, 0.65 nm, and 1.30 nm for SrRuO$_3$, Sr$_{0.67}$Ca$_{0.33}$RuO$_3$, Sr$_{0.33}$Ca$_{0.67}$RuO$_3$, and CaRuO$_3$, respectively. Different microstructures, such as step-like (SrRuO$_3$, Sr$_{0.33}$Ca$_{0.67}$RuO$_3$) and spiral-like (Sr$_{0.67}$Ca$_{0.33}$RuO$_3$), were observed. More importantly, the grain sizes varied significantly in different buffer layers (larger in SrRuO$_3$, Sr$_{0.67}$Ca$_{0.33}$RuO$_3$, and smaller in Sr$_{0.33}$Ca$_{0.67}$RuO$_3$, CaRuO$_3$) and the larger grain sizes in the buffer layers could facilitate BFO film growth.

Figure 4 shows the I-V curves of the BFO films. The measurement setup is shown in the inset to Figure 4(a). The leakage currents in the BFO film on SrRuO$_3$ are much smaller than those with other buffer layers. At the maximum electrical field (8 V–210 kV/cm), the leakage current in the film on the SrRuO$_3$-buffer layer was $1.02 \times 10^{-3}$ A/cm$^2$, while for the film on the Sr$_{0.33}$Ca$_{0.67}$RuO$_3$-buffer layer was $27.2 \times 10^{-3}$ μA/cm$^2$. The maximum leakage currents in different samples are summarized in the inset to Figure 4(c). The polarization reversal currents ($\sim 10$ μA/cm$^2$) contributed little to the measured leakage currents ($10^3$–$10^4$ μA/cm$^2$). Their effects can be excluded. The sheet resistances of the underlying buffer layers were 9 Ω, 19 Ω, 12 Ω, and 35 Ω for SrRuO$_3$, Sr$_{0.67}$Ca$_{0.33}$RuO$_3$, Sr$_{0.33}$Ca$_{0.67}$RuO$_3$, and CaRuO$_3$, respectively. The values are comparable with the published data. The resistance of the CaRuO$_3$-buffer layer is much larger than the resistance of the other buffer layers,
which could affect the I-V behaviors of the BFO films. Such effects need further investigations.

The most interesting feature of these I-V curves is the highly asymmetric or diode-like I-V behaviors observed in the films grown on SrRuO$_3$, Sr$_{0.67}$Ca$_{0.33}$RuO$_3$, and Sr$_{0.33}$Ca$_{0.67}$RuO$_3$-buffer layers. However, the I-V curves for the film grown on the CaRuO$_3$-buffer layer under positive or negative electrical bias are almost symmetric. Such asymmetric I-V characteristics have been observed in many metal-ferroelectric-metal and metal-ferroelectric-semiconductor-metal configurations. Different top and bottom electrodes may be the origin of these highly asymmetric I-V behaviors, as previously demonstrated in Au-BFO-ZnO, Pt-BaTiO$_3$-ZnO, Au-(Pb,La)(Zr,Ti)O$_3$-SrTiO$_3$:Nb, and Pt-BFO-SRO (Refs. 37 and 38) heterostructures. In current configurations, i.e., Au-BFO-SCRO, these different bottom and top electrodes can also lead to highly asymmetric I-V behaviors, as two p-n junctions connected back-to-back (as discussed below).

Another intriguing point is the nonconformity of the leakage currents during field-increasing or “forward sweep” and field-decreasing or “reverse sweep” (hysteresis behavior). The nonconformity is considered to be related to ferroelectric polarization states. Some reports on resistance switching and rectifying diode effects in ferroelectric capacitors suggest that the resistivity of the metal/ferroelectric/metal structure is indeed affected by the polarization states. In BFO films, it was found that the BFO-electrode interface barrier could be changed (increased or decreased) by the ferroelectric

![AFM images of buffer layers](image1)

**FIG. 3.** AFM images of buffer layers (a) SrRuO$_3$, (b) Sr$_{0.67}$Ca$_{0.33}$RuO$_3$, (c) Sr$_{0.33}$Ca$_{0.67}$RuO$_3$, and (d) CaRuO$_3$.

![Leakage currents in BFO thin films](image2)

**FIG. 4.** Leakage currents in BFO thin films on different buffer layers of (a) SrRuO$_3$, (b) Sr$_{0.67}$Ca$_{0.33}$RuO$_3$, (c) Sr$_{0.33}$Ca$_{0.67}$RuO$_3$, and (d) CaRuO$_3$. The measurement step is 0.2 V with a delay time of 2 s. The inset in (a) illustrates the I-V measurement configurations. Inset in (c) shows the maximum leakage current at +8 V of all films on different buffer layers.
polarization through the effects of polarization charges.\textsuperscript{38,41} The conduction in BFO films was considered to be p-type, which was induced by Bi-loss (like acceptor doping) during film formation at high temperature.\textsuperscript{44} Under positive bias, the interface between BFO and the bottom SCRO electrode is in the “non-blocking” state (like a forward-biased p-n junction), while the interface between BFO and the top Au electrode is in the “blocking” state (like a reverse-biased p-n junction). Therefore, the leakage current in a SCRO-BFO-Au structure is dominated by the “blocking” BFO-Au interface. Similarly, under negative bias, the leakage is governed by the BFO-SCRO interface. Considering that the polarization state under positive bias, during forward sweep ($0 \,\text{V} \rightarrow +8 \,\text{V}$), the polarization is initially upwards (pointing to top electrode, defined as “+P”) and then switches to downwards (+P) during the reverse sweep ($+8 \,\text{V} \rightarrow 0$). Moreover, for downwards polarization (+P), the polarization during field-decreasing ($+8 \,\text{V} \rightarrow V_c$) is larger than that during field-increasing ($V_c \rightarrow +8 \,\text{V}$) (this holds for a real ferroelectric capacitor; for an ideal one, they are equal). When the polarization direction is −P, positive polarization charges accumulate at the BFO-Au interface, which will increase the potential barrier for the charge carrier (hole) injection from the Au electrode (“repel holes”). When the polarization switches to +P, negative polarization charges appear at the BFO-Au interface, which will then lower the potential barrier (“attract holes”). The +P polarization is larger under reverse sweep as stated above, and the potential barrier will be lower. Therefore, the leakage current is larger during the reverse sweep due to the lower interface barrier. The band diagrams under a positive bias with −P and +P are shown in Figures 5(a) and 5(b), respectively. The built-in potential barrier can thus be changed by the ferroelectric polarization by \textsuperscript{38,41}

$$\Delta \phi_{bi} = \frac{SP}{\varepsilon_0 \varepsilon_r},$$

where P is the ferroelectric polarization, δ is the thickness of the interface layer between the surface polarization charge and the electrode, $\varepsilon_0$ is the vacuum permittivity, and $\varepsilon_r$ is the static dielectric constant of the film. Wang \textit{et al.} obtained a $\Delta \phi_{bi}$ of 1.38 eV using $P = 60 \,\mu\text{C/cm}^2$, $\delta = 1 \,\text{nm}$, $\varepsilon_r = 50$, for a 240 nm BFO film in a Pt-BFO-SRO structure prepared by PLD,\textsuperscript{37} while Lee \textit{et al.} calculated $\Delta \phi_{bi}$ to be 0.6 eV using $P = 65 \,\mu\text{C/cm}^2$, $\delta = 1 \,\text{nm}$, $\varepsilon_r = 100$, for a 400 nm BFO film in a Pt-BFO-SRO structure deposited by sputtering.\textsuperscript{38} In our case, P is only $15.5 \,\mu\text{C/cm}^2$ for the Au-BFO-SRO sample. The change in the potential barrier would therefore be expected to be 0.1–0.4 eV. The potential barrier height without charges at the interface is expected to be ~0.6 eV, which depends on the density of impurities in the film, especially around the interface region.\textsuperscript{41} Next, we consider the case of negative biases, where the interface between BFO and Au is “non-blocking” and that between BFO and SCRO is “blocking.” In the same way, the leakage current during forward sweep ($0 \rightarrow -8 \,\text{V}$) is lower than that during reverse sweep ($-8 \,\text{V} \rightarrow 0$). However, compared with the case of positive biases, suppressed hysteresis and much lower leakage currents are observed, which indicates a higher potential barrier at the BFO-SCRO interface under negative bias than that at the BFO-Au interface under positive bias. The higher barrier may be induced by the accumulated positively charged oxygen vacancies ($V_{o}$) at the BFO-SCRO interface due to the self-poled upwards polarization (parallel with −P): a negative polarization charge is built up near the bottom SCRO electrode, which attracts $V_{o}$ to migrate towards the SCRO electrode at high temperatures during deposition.\textsuperscript{41} A rough interface may facilitate the accumulation of these oxygen vacancies. The roughness of the SRO bottom

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{band_diagrams.png}
\caption{Band diagrams for the BFO-Au interface under positive (a) forward, (b) reverse bias and the BFO-SCRO interface under negative (c) forward, and (d) reverse bias. The applied field (positive or negative) is at the top Au electrode. $E_F$: Fermi level, VB: valence band, $V_{C}$: positively charged oxygen vacancies, $\phi_{Bi-Au}$: built-in potential barrier at the BFO-Au interface with the ferroelectric polarization inside the film pointing to the top Au electrode ($-P$), $\phi_{Bi-SCRO}$: built-in potential barrier at the BFO-SCRO interface with the ferroelectric polarization inside the film pointing to the bottom SCRO electrode ($+P$).}
\end{figure}
electrode (1.79 nm) is the greatest among all the SCRO electrodes and the film on the SRO electrodes exhibits the most striking asymmetric I-V behavior. These localized permanent positive charges lead to the formation of a high potential barrier at the SCRO-BFO interface for the positive charge carriers (holes), as shown in Figures 5(c) and 5(d). The barrier height is so large that it overtakes the effects of the ferroelectric polarization charges. Therefore, the leakage current under negative bias is much smaller and the hysteresis is also not that exaggerated. This scenario also accounts for the asymmetric I-V behaviors.

Several types of leakage or conduction mechanisms may contribute the leakage current, including Ohmic conduction, space-charge-limited-conduction (SCLC), interface-limited Schottky emission, bulk-limited Poole-Frenkel (PF) emission, interface-limited Fowler-Nordheim (FN) tunneling, and hopping conduction (HC). These mechanisms can be described by the following equations,

\[ J_{SCLC} = \frac{9 \mu e_0 e_r}{8d^2} E^n, \]

where \( d \) is the film thickness, \( \mu \) is the charge carrier mobility, \( e_0 \) is the vacuum permittivity, \( e_r \) is the relative dielectric constant of the film, \( E \) is the electrical field, \( J \) is the current density, \( n = 2 \) for trap-free conditions, \( n > 2 \) for SCLC with charge carrier traps;

\[ J_{Schottky} = A T^2 e^{-\frac{e_0}{q} \sqrt{\frac{\Phi_a}{K_T}}}, \]

where \( A \) is constant, \( \Phi_a \) is the Schottky barrier, \( T \) is the absolute temperature in Kelvin, \( q \) is the elementary charge, \( K_T \) is the Boltzmann constant;

\[ J_{PF} = B E e^{-\frac{e_0}{q} \sqrt{\frac{\Phi_i}{K_T}}}, \]

where \( B \) is constant and \( \Phi_i \) is the trap ionization energy;

\[ J_{FN} = C E^2 e^{-\frac{e_0}{q} \sqrt{\Phi_i}}, \]

where \( C \) and \( D \) are constants and \( \Phi_i \) is the potential barrier height;

By fitting the experimental data in the coordinates of \( \ln(J) \) vs. \( \ln(E) \) (SCLC or Ohmic), \( J/T^2 \) vs. \( E^{0.5} \) (Schottky), \( J/E \) vs. \( E^{0.5} \) (PF), \( J/E^2 \) vs. \( E^{0.5} \) (FN), and \( \ln(J) \) vs. \( E \) (Hopping), it is possible to determine which mechanisms contribute to the leakage currents. In all BFO films, SCLC dominated the leakage currents under a high electrical field and Ohmic conduction under a low electric field. The conduction mechanisms under a negative bias resembled those under a positive bias. The slope (\( n \)) of the \( \ln(J) \)–\( \ln(E) \) plot in the SCLC region was found to be 1.7–3.0, deviating from the ideal value of 2. This is related to the distribution of the charge carrier traps in the bandgap, which depends on the applied field. One example of these fittings is shown in Figure 6 for the BFO on \( \text{Sr}_{0.22}\text{Ca}_{0.78}\text{RuO}_3 \). The filled traps level was also observed, where \( n \) was much larger than 2 (6.4 and 5.5 as shown in Figure 6). The physical nature of the charge carrier traps is believed to be the structural defects or impurities, for example the cation/anion vacancies.

The ferroelectric hysteresis loops of the films are shown in Figure 7. All films exhibited well-defined loops. However, the films grown on \( \text{Sr}_{0.22}\text{Ca}_{0.78}\text{RuO}_3 \)-buffer layer exhibited a rounded shape, indicating considerable contribution from leakage currents. The remnant polarization (\( P_r \)) and coercive field (\( E_c \)) in the film on the \( \text{SrRuO}_3 \)-buffer layer are 15.5 \( \mu \text{C/cm}^2 \) and 176 kV/cm, respectively.

\[ J_{Hopping} = qanv e^{-\frac{e_0}{q} \sqrt{\frac{\Phi_i}{k_BT}}}, \]
The small $P_c$, compared with other BFO films (~50–130 μC/cm² (Refs. 1, 5, 6, and 9)), may be due to the secondary phase or smaller grain size in our samples, as shown in Figure 1(a).

The piezoelectric responses of the films are shown in Figures 8 and 9. Figure 8 shows the piezoelectric force microscopy (PFM) phase pictures of non-poled films. Large ferroelectric domains are clearly observed in the BFO films.

The piezoelectric responses of the films are shown in Figures 8 and 9. Figure 8 shows the piezoelectric force microscopy (PFM) phase pictures of non-poled films. Large ferroelectric domains are clearly observed in the BFO films.
grown on SrRuO$_3$ and Sr$_0.67$Ca$_{0.33}$RuO$_3$-buffer layers. The domain sizes are much smaller and the contrast between different domains is blurred in these two samples. Two factors may account for these differences: the film orientation and grain size. As shown previously, the films grown on SrRuO$_3$ and Sr$_0.67$Ca$_{0.33}$RuO$_3$-buffer layers are highly (001) oriented and exhibit larger grain sizes (260 nm and 207 nm). The (110) orientation was observed in the other two samples, even at a low percentage and the grain sizes are also smaller (186 nm and 134 nm). However, the piezo-response (amplitude) is the largest in the film grown on the Sr$_0.33$Ca$_{0.67}$RuO$_3$-buffer layer, which is 0.233 V under an applied field of 10 V. The corresponding values for the films on SrRuO$_3$, Sr$_0.67$Ca$_{0.33}$RuO$_3$, and CaRuO$_3$-buffer layers are 0.167 V, 0.184 V, and 0.172 V, respectively, as shown in Figure 8. Another interesting point observed in Figure 9 is the smaller local coercive fields in the sample grown on Sr$_0.33$Ca$_{0.67}$RuO$_3$ and CaRuO$_3$-buffer layers, which are 0.49 V and 0.40 V compared with 0.62 V in BFO-SrRuO$_3$ and 1.21 V in BFO-Sr$_0.67$Ca$_{0.33}$RuO$_3$. This difference may be related to the larger lattice-mismatch strains in the films on Sr$_0.33$Ca$_{0.67}$RuO$_3$ and CaRuO$_3$ buffer layers, as discussed previously. The large strain will deform the crystal structure of BFO from rhombohedral to tetragonal to some extent and then improve the piezoelectric (d$_{33}$) and ferroelectric (P$_{r}$ and E$_{c}$) properties. In our case, the structural differences cannot be determined as their XRD diffraction peaks are overshadowed by the buffer layers. But the lattice constants of the films with different buffer layers are indeed different, as shown in the XRD results. Therefore, we may expect lattice deformation in films with larger strains and therefore enhanced piezoelectric performance. The final point worth mentioning is the much smaller coercive fields (0.40–1.21 V) measured by local PFM compared with those (6.69–12.49 V, see Figure 7) obtained from the ferroelectric hysteresis measurements. The origin for this may be (1) the smaller electrode area (~20 nm in diameter) of the PFM tip, which could induce enhancement of a localized electrical field due to the sharpness of the tip and the tip-contact geometry, and (2) the non-ferroelectric secondary phases (as shown in Figure 1(a)), which will hinder the polarization reversal in larger area (2 $\times$ 10$^5$ nm in diameter) measurements and may not manifest itself in the local (20 nm in diameter) PFM measurements.

CONCLUSIONS

Effects of buffer layers (SrRuO$_3$, Sr$_0.67$Ca$_{0.33}$RuO$_3$, Sr$_0.33$Ca$_{0.67}$RuO$_3$, CaRuO$_3$) on the microstructural, crystallographic, electrical, ferroelectric, and piezoelectric properties of (001)-oriented BFO thin films were systematically studied. It was found that the lattice constants of the BFO films changed gradually as the buffer layer was varied from SrRuO$_3$ to CaRuO$_3$. Diode behavior in the I-V curves was observed in the BFO films on SrRuO$_3$, Sr$_0.67$Ca$_{0.33}$RuO$_3$, Sr$_0.33$Ca$_{0.67}$RuO$_3$-buffered layers. Space-charge-limited-conduction mechanism was verified in the leakage of all the films. The film on SrRuO$_3$ exhibited the lowest leakage current and a well-saturated ferroelectric hysteresis loop. Different piezoelectric responses, revealed by PFM method, were observed in these films. BFO films with larger strains showed increased piezo responses. Different strain states in these films may account for these observations.

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