The dependence of oxygen vacancy distributions in BiFeO$_3$ films on oxygen pressure and substrate

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The epitaxial (001)-oriented 250 nm BiFeO$_3$/50 nm SrRuO$_3$ films were deposited on DyScO$_3$ and SrTiO$_3$ substrates, respectively. Following the growth, the cooling in lower oxygen pressure results in the creation of oxygen vacancies at the surface of the BiFeO$_3$ film and the epitaxial strain drives these vacancies to diffuse from the film surface to the film interface. The SrTiO$_3$ substrate strongly absorbs oxygen vacancies from the BiFeO$_3$ film while the DyScO$_3$ substrate does not. Therefore, the depth distribution of oxygen vacancies depends on the oxygen pressure during cooling, the epitaxial strain, and the substrate absorbing oxygen vacancies. 

The study of oxygen vacancies ($V_{O\delta}$) is very important for dielectric, ferroelectric, piezoelectric, or multiferroic ABO$_{3-\delta}$ ($\delta$ expresses the density of $V_{O\delta}$) oxides that can be used in microelectronics, sensors, and other devices. On one hand, even a low density of $V_{O\delta}$ may greatly increase leakage currents, relax strain, or even diminish ferroelectric properties in epitaxial BiFeO$_3$-$\delta$ films. On the other hand, leaky BiFeO$_3$-$\delta$ also shows many wonderful properties such as photovoltaic effect. Although these $V_{O\delta}$ in intergaps have been extensively studied, the mechanism of the formation of low-density distributions of $V_{O\delta}$ is not clear in BiFeO$_3$-$\delta$ and SrTiO$_3$-$\delta$.

Positron annihilation, on the other hand, can nondestructively trace the depth-profile (from surface to >1 mm) distribution of such low-density vacancies. A positron can annihilate with an electron in heterostructures, emitting two $\gamma$ rays with the energy ($E_\gamma$) of $\sim$511 keV. With a monoenergetic positron beam, the parameter ($S$) of positron annihilation can be measured as a function of the incident positron energy ($E$, keV), where $S$ is defined as $S=N_i/N_T$, and $N_i$ and $N_T$ are the numbers of annihilation events occurring in the range of 503.8 keV $\leq E_\gamma \leq 511.2$ keV or 510.24 keV $\leq E_\gamma \leq 511.76$ keV, respectively. Compared with the $S$ of vacancy-free material, the $S$ of a material may increase when open volume and/or density of vacancy-type defects increase.

In this article, we have found that the partial pressure of oxygen ($P_{O_2}$) during cooling after growth, strain-state, and substrate material are very important in manipulating the density, diffusion, and distribution of $V_{O\delta}$.

Using pulsed laser deposition, 250 nm BiFeO$_3$-$\delta$ (BFO) and 50 nm SrRuO$_3$-$\delta$ (SRO) films (used as a bottom electrode) were epitaxially grown on (110)-DyScO$_{3-\delta}$ (DSO), starting $\delta$=0 and (001)-SrTiO$_3$ (STO, starting $\delta$=0) single crystal substrates at 700 °C and 0.1 Torr $P_{O_2}$. Following growth, these samples were then cooled to room temperature at 5 °C/min in 760, 0.1, or 0.001 Torr $P_{O_2}$ in order to induce different $\delta$ for BiFeO$_3$-$\delta$, SrRuO$_3$-$\delta$, or SrTiO$_3$-$\delta$. Henceforth, we will refer to these samples as 760-, 0.1-, and 0.001-BFO/SRO/STO; and 760-, 0.1-, and 0.001-BFO/SRO/DSO. The crystal structure and strain of the samples were studied using x-ray diffraction (XRD). The density and distribution of $V_{O\delta}$ was estimated by positron annihilation. The $S$ was analyzed by the VEPFIT method $S(E)=S_iF_i(E)+\sum S_jF_j(E)$, where $F_i(E)$ is the fraction of positrons annihilated at the surface and $F_j(E)$ is that in the $i$th layer, $S_i$ and $S_j$ are the $S$ parameters corresponding, respectively, to the annihilation of positrons on the surface and that in the $i$th layer. Three layers were chosen for all samples except two layers for 0.1-BFO/SRO/STO, and one fixed boundary at 300 nm was used during simulation. BFO surfaces were studied using atomic force microscopy (AFM) and ferroelectric domains of the BFO films were studied using piezoelectric force microscopy (PFM). Other electric properties of similar samples were already reported in Refs. 2 and 3.

The evolution of strain in the BFO/SRO/DSO and BFO/SRO/STO heterostructures was studied by XRD patterns in Fig. 1. When there is no epitaxial strain, the pseudocubic crystal lattice is $\sim$0.3922 nm for SRO ($\delta$=0) thick film, $\sim$0.3906 nm for STO ($\delta$=0) crystal substrate, $\sim$0.3948 nm for DSO ($\delta$=0) crystal substrate, and $\sim$0.3965 nm for BFO ($\delta$=0) crystal. The 002 diffraction peaks of the BFO film were observed at larger angles for BFO/SRO/DSO in Fig. 1(a) compared to those of BFO/SRO/STO in Fig. 1(b), providing evidence for smaller compressive strain in BFO films of BFO/SRO/DSO than those of BFO/SRO/STO. For 760- and 0.1-BFO/SRO/DSO (or 0.001-BFP/SRO/DSO), the 002 diffraction peaks of BFO film are slightly higher than (or close to) the 45.770° expected for BFO ($\delta$=0) crystal [inset of Fig. 1(a)], suggesting that the 250 nm BFO films are weakly strained (or is essentially relaxed by a higher $\delta$). This suggestion is consistent with the fact that the full width at half maximum (FWHM) of 002 diffraction peak of DSO is narrowest in 0.001-BFP/DSO. For 760-, 0.1-, and 0.001-BFO/SRO/STO in the inset of Fig. 1(b), the 002 dif-
that a large amount of FWHM than those of 760-, 0.1-BFO/SRO/STO, suggesting layer of 0.001-BFO/SRO/STO shows a little larger 2 
substrate in all BFO/STO/STO samples. Besides, the STO 
the compressive strain between the BFO film and the STO 
relate to the increasing ionic radii of Ti ions with decreasing 

FIG. 1. (Color online) XRD patterns for (a) BFO/SRO/DSO and (b) BFO/ 
SRO/STO, where the 002 peaks are amplified in insets and the dashed lines 
located at 45.770° expected for bulklike BFO.

fraction peaks of BFO films can be fitted by a peak with 
2θ_{002} ≤ 45.390°, i.e., c axis of >0.3996 nm, which suggests 
that the density of V_{0S} is not high enough to effectively relax 
the compressive strain between the BFO film and the STO 
substrate in all BFO/STO/STO samples. Besides, the STO 
layer of 0.001-BFO/SRO/STO shows a little larger 2θ_{002} and 
FWHM than those of 760-, 0.1-BFO/SRO/STO, suggesting 
that a large amount of V_{0S} diffused to STO, and then induced 
the lightly expanded c axis. This chemical expansion should 
relate to the increasing ionic radii of Ti ions with decreasing 
oxidation state from +4 to +3.

In Fig. 2, the S-E curves of the three BFO/SRO/DSO and 
three BFO/SRO/STO heterostructures can be treated as 
four regions as a whole. A mean implantation depth (Z, nanometer) can be estimated according to $Z = 27.5 \cdot E^{1.1}/p$ (unit of $p$ is g/cm$^2$), for example, Z = 240 nm for 12.5 keV and 
Z = 330 nm for 15 keV. The highest S value observed at $E < 2.7$ keV (i.e., region A with Z between 0 and 20 nm) is mainly contributed by surface effects because some positrons 
implanted to the near-surface BFO can be reflected back and 
then annihilate at the surface. The S show a lowest value or 
turning point at ~2.7 keV, suggesting that the surface effect 
can be ignored at $E > 2.7$ keV. The $S$ value at $E$ ranging from ~2.7 to ~12 keV (i.e., region B with Z between 20 and 
230 nm) is mostly contributed by BFO film and can be treated as the characteristic S of BFO (i.e., $S_{BFO}$). The $S$ 
value at E between 12 and 15 keV (i.e., region C with Z between 230 and 330 nm, compared with Z between 250 and 
300 nm for SRO layer) may be cocontributed by BFO, 
SRO, or substrate, where the boundaries of $E > 12$ and $E < 15$ keV are roughly estimated and their precision do not 
influence the following analyses. The $S$ value at $E > 15$ keV (i.e., region D with Z > 330 nm) is contributed by STO 
or substrate, and it can be treated as the characteristic S of STO (i.e., $S_{STO}$) or DSO (i.e., $S_{DSO}$). The characteristic S value 
of BFO, SRO, DSO, and STO were also roughly estimated by 
VEPFIT method and the results were also shown in Fig. 2 for 
comparison. Therefore, the $S$ value at regions B and D can be treated as $S_{BFO}$, $S_{STO}$, or $S_{DSO}$ directly, and the large fluctuation 
of $S_{BFO}$ in the B region suggests that the distribution of 
$V_{0S}$ is not homogenous in BFO films.

For the three BFO/SRO/DSO heterostructures [Figs. 2(a)–2(c)], the distributions of $V_{0S}$ in the BFO films can be 
explained according to the cooling $P_{O_2}$ and strain. The $S_{DSO}$ at region D is ~0.431 for 760-, 0.1-, and 0.001-BFO/SRO/ 
DSO, suggesting that DSO absorbs few $V_{0S}$ from the BFO/ 
SRO films regardless of the variation in $P_{O_2}$ from 760 to 
0.001 Torr. This is consistent with the previous report that 
the highest breakdown field of 8 MV/cm was obtained in 
10-nm-thick DyScO$_3$ films grown on Nb-SrTiO$_3$ substrate at 
10-nm thick DyScO$_3$. For the three BFO/SRO/DSO heterostructures [Fig. 2(d), the $S_{BFO}$ at $E$ = 12 keV is lower than the $S_{BFO}$ at $E$ = 2.7 keV in region B, and the $S_{STO}$ is lower than the other two $S_{STO}$ of 0.1- and 0.001-BFO/SRO/STO in region D. Although the stronger compressive strain in 760-BFO/STO/STO should induce $V_{0S}$ to diffuse from the BFO surface to 
the BFO/SRO interface, the variation between 760-BFO/ 
SRO/STO and 760-BFO/SRO/DSO should not only come 
from their different strain-states as set by the substrate. The $S_{STO}$ in region D increases as the cooling $P_{O_2}$ is lowered 
from 760 to 0.001 Torr in the three BFO/SRO/STO, suggesting 
that the STO substrate does absorb $V_{0S}$ from BFO/SRO 
films. It suggests that STO owes a lower energy of oxygen 
vacancies formation than that of DSO. Ti atoms allow Ti$^{3+}$ 
and Ti$^{4+}$ as their stable ion states, thus the transformation 

FIG. 2. (Color online) The $S$-$E$ curves (open square), their simulations using 
VEPFIT method (black line for fitting $S$ and gray lines for the estimated 
characteristic $S$ of each layer), and the four regions divided by red dot lines 
of (a) 760-, (b) 0.1-, (c) 0.001-BFO/SRO/DSO, and (d) 760-, (e) 0.1-, and (f) 
0.001-BFO/SRO/STO.
from Ti$^+$ to Ti$^{3+}$ was induced to keep charge equilibrium when V$_{OS}$ was produced. Therefore, the near-interface BFO layer is found to lose a large proportion of the V$_{OS}$ due to STO absorbing V$_{OS}$ in the 760-BFO/SRO/STO heterostructure since not enough V$_{OS}$ were produced at BFO surface to offset such a loss. As a result the bottom BFO layer shows the lowest S$_{BFO}$ at B region.

For the 0.1-BFO/SRO/STO heterostructure [Fig. 2(e)], S$_{BFO}$ at $E\sim$ 2.7 keV change a little, while both the S$_{BFO}$ at $E\sim$ 12 keV in region B and the S$_{STO}$ in region D obviously increase compared with those in 760-BFO/SRO/STO. The STO appears to have absorbed many V$_{OS}$ from the near-interface BFO to increase its S$_{STO}$. At the same time it appears that a nearly equal amount of V$_{OS}$ were created at the BFO surface because of the decrease in P$_{O_2}$. Finally, these surface V$_{OS}$ are thought to have diffused to the near-interface BFO because of the strong compressive strain from the STO substrate.

For the 0.001-BFO/SRO/STO heterostructure [Fig. 2(f)], the S$_{BFO}$ in B region and S$_{STO}$ in region D are higher than the corresponding S$_{BFO}$ and S$_{STO}$ in 760 and 0.1-BFO/SRO/STO [Figs. 2(d) and 2(e)]. The low cooling P$_{O_2}$ (0.001 Torr) induced a large amount of V$_{OS}$ to form at the surface of the BFO, which then diffuse to the near-interface BFO layer and the STO substrate. However, the S$_{BFO}$ in B region and S$_{STO}$ in region D are far lower than those of the strain-relaxed 0.001-BFO/SRO/DSO, thus the density of V$_{OS}$ in BFO are not high enough to relax the strain between BFO and STO which is also confirmed by XRD pattern (Fig. 1).

The topographies of BFO surface relate to the S$_{BFO}$ in B region and the S$_{STO}$ or S$_{DSO}$ in region D. Lower P$_{O_2}$ during cooling worsens the surface of the BFO film for the three BFO/SRO/DSO heterostructures [Figs. 3(a)–3(c)]. When the films were cooled at lower P$_{O_2}$, more V$_{OS}$ form in BFO/SRO films and more O$_2$ are evolved from the BFO surface. V$_{OS}$ change the crystal structure and therefore change the surface morphology of BFO films. At 760, 0.1, or 0.001 Torr cooling P$_{O_2}$, BFO/SRO/STO heterostructure [Figs. 3(d)–3(f)] shows worse BFO surfaces than BFO/SRO/DSO, respectively. Further, decreasing the cooling P$_{O_2}$ also worsens the BFO surface of BFO/SRO/STO faster than that of BFO/SRO/DSO.

For BFO/SRO/STO, their rougher surface should be due to their differences from BFO/SRO/DSO, i.e., the stronger compressive strain and/or the STO absorbing V$_{OS}$. As mentioned before, with the P$_{O_2}$ decreasing from 760 to 0.001 Torr, BFO surface creates a large amount of V$_{OS}$ to satisfy the increased S$_{STO}$ in region D. Simultaneously, a large amount of oxygen atoms in STO substrate diffused to BFO surface and contribute more O$_2$. These V$_{OS}$ diffusion, together with the V$_{OS}$-induced crystal expansion, should be the main reason of the BFO surface worsening.

In PFM in-plane images, all BFO films studied were found to show similar ferroelectric domain structures. As an example, in-plane PFM images of 0.1-BFO/SRO/DSO and 0.1-BFO/SRO/STO are shown in Figs. 3(g) and 3(h), respectively.

During the cooling of the sample, the lower partial pressure P$_{O_2}$ helps the BFO surface to create additional V$_{OS}$, the epitaxial strain from substrate always drive these V$_{OS}$ to the BFO/SRO interface, the STO substrate strongly absorb V$_{OS}$ from BFO films in BFO/SRO/STO samples while DSO substrate does not absorb V$_{OS}$ in BFO/SRO/DSO samples. The above three reasons contribute to several different depth distributions of V$_{OS}$ and different surface roughness that can influence application of BFO films.

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