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Letter

# A giant polarization value in bismuth ferrite thin films

Yuanyu Wang

*College of Materials Science and Metallurgy Engineering, Guizhou University, Guiyang 550003, PR China*

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ABSTRACT

An approach is used to improve the remanent polarization of $BiFeO_3$ thin films, where the $BiFe_{0.96}Zn_{0.04}O_3$ thin film with (1 1 1) orientation was grown on the $SrRuO_3/SrTiO_3$(1 1 1) substrate by rf sputtering. A higher dielectric constant and a lower dielectric loss are demonstrated for the $BiFe_{0.96}Zn_{0.04}O_3$ thin film as compared with those of pure $BiFeO_3$ thin film. The introduction of Zn deteriorates the magnetic properties of BFO thin films. A giant polarization value of $2P_r \sim 268.5\ \mu C/cm^2$ is induced for the $BiFe_{0.96}Zn_{0.04}O_3$ thin film as confirmed by PUND, owing to the (1 1 1) orientation, the introduction of Zn, and a low leakage current density.



$BiFeO_3$ (BFO) with a rhombohedrally distorted perovskite structure has been recently given to much attention because of its large polarization value, a high Curie temperature ($T_C \sim 1104$ K), and G-type antiferromagnetic ($T_N \sim 644$ K) behavior at above room temperature [1–6], which promises as a candidate material for the high-density ferroelectric random access memory and several other technologically demanding applications [1,2]. However, its higher leakage current density at room temperature seriously hinders the potentially feasible applications that have been considered for the BFO thin films [7].

Several different measurements have been conducted for improving the ferroelectric properties of BFO thin films by reducing the leakage current density at room temperature, such as the employment of a single crystal substrate [3,8], the use of an appropriate buffer layer [9–11], the construction of a multilayer structure [12,13], and the cation substitutions for the Bi and Fe sites in the crystal structure [14–17]. However, the ferroelectric properties are not ideal for the BFO thin films except for the use of a single crystal substrate together with the orientation modification [3,8]. A remnant polarization of $P_r \sim 55\ \mu C/cm^2$ was observed for the (1 0 0)-oriented BFO thin film deposited on the $SrRuO_3/SrTiO_3$(1 0 0) substrate [3]. Moreover, a larger polarization of $P_r \sim 100\ \mu C/cm^2$ has been induced for the (1 1 1)-oriented BFO thin film deposited on the $SrRuO_3/SrTiO_3$(1 1 1) substrate [8]. The Zn – modified BFO thin film with a polycrystalline perovskite grown on the $Pt/TiO_2/SiO_2/Si$(1 0 0) substrate has exhibited a large remanent polarization of $P_r \sim 73\ \mu C/cm^2$ when measured at the low temperature of 80 K, but it is very difficult to get good $P$–$E$ loops at room temperature due to the involvement of a high leakage current density [15]. Moreover, a giant remanent polarization value of $P_r \sim 146\ \mu C/cm^2$ is only obtained for the BFO thin film with a tetragonal structure when measured at a low temperature of 90 K [18]. Therefore, it seems very difficult to exceed this polarization value for the BFO thin films when measured at room temperature, and even there are few reports on a polarization value of $P_r > 100\ \mu C/cm^2$ for the BFO thin film when measured at room temperature.

In the present work, we hope to further improve the ferroelectric properties of bismuth ferrite thin films by combining the site engineering, the single crystal substrate, and the orientation modification, where the $BiFe_{0.96}Zn_{0.04}O_3$ (BFZO) thin film with (1 1 1) orientation was grown on the $SrRuO_3/SrTiO_3$(1 1 1) substrate by radio frequency (rf) sputtering. Its ferroelectric properties were tailored, and a giant polarization value of $2P_r \sim 268.5\ \mu C/cm^2$ has been induced for the BFZO thin film, owing to a (1 1 1) orientation, the introduction of Zn, and a low leakage current density. It is a promising way to further improve the ferroelectric properties of bismuth ferrite thin films.

$BiFe_{0.96}Zn_{0.04}O_3$ thin films were deposited by rf sputtering, where the ceramic targets of $SrRuO_3$ and $Bi_{1.10}(Fe_{0.95}Zn_{0.05})O_3$ were synthesized by the solid state reaction. The oxide mixture of $Bi_{1.10}(Fe_{0.95}Zn_{0.05})O_3$ was calcined at ~700 °C in air for 3 h to form the desired phase, and followed by sintering at ~800 °C for 2 h. The $SrRuO_3$ buffer layer was firstly grown on the $SrTiO_3$(1 1 1) substrate at the substrate temperature of ~650 °C, and the BFZO thin film was then deposited on the $SrRuO_3/SrTiO_3$(1 1 1) substrate at the substrate temperature of ~620 °C. They were deposited under a rf power of ~80 W, and at a deposition pressure of ~1.0 Pa with Ar and $O_2$ at a ratio of 4:1. The chemical composition of $BiFe_{0.96}Zn_{0.04}O_3$ thin films is confirmed by the energy dispersive

*E-mail address:* yuanyuwang0216@163.com

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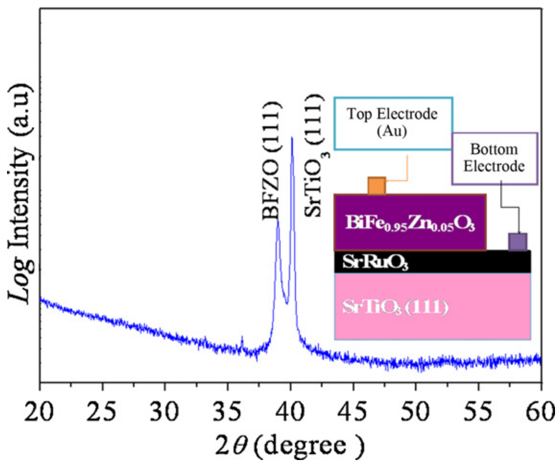


**Fig. 1.** XRD pattern for the BFZO thin film deposited on the $SrRuO_3/SrTiO_3(1\,1\,1)$ substrate, where the insert is diagram for the $Au/BFZO/SrRuO_3$ capacitor.

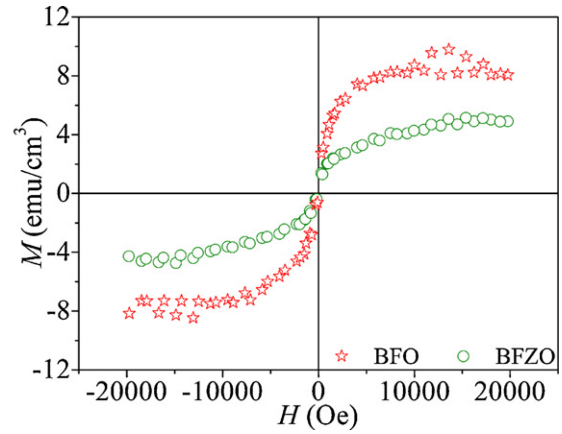


**Fig. 3.** *M–H* curves of BFO and BFZO thin films.

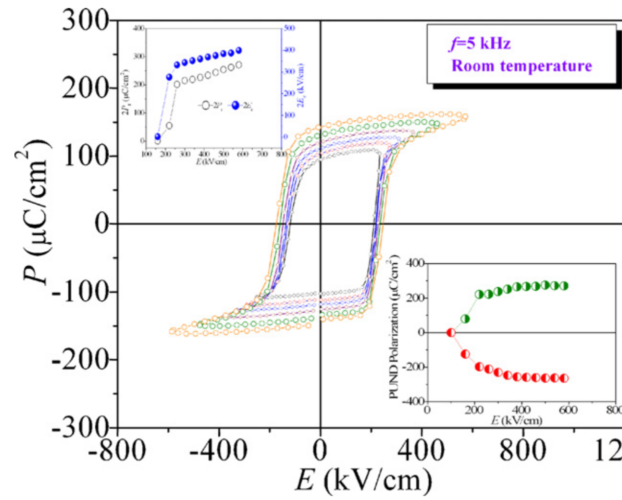


**Fig. 4.** *P–E* loops for the BFZO thin film deposited on the $SrRuO_3/SrTiO_3$ substrate, where the inserts are $2P_r$ and $2E_c$ values as a function of driving electric fields as well as PUND measurement.

X-ray spectroscopy (EDX). Circular Au electrodes of 0.10 mm in diameter were sputtered on the film surface using a shadow mask in order to investigate the electrical properties of the thin films.

The phases of thin films were analyzed by using X-ray diffraction (XRD) (DX-1000, Dangdong, PR China). Magnetic properties of thin films were measured by using the superconducting quantum interference device. Their ferroelectric behavior was studied by the Radiant precise workstation (RT2000 Tester, USA). An HP 4294 analyzer was used to characterize the dielectric behavior. The leakage current was measured by using a Keithley meter (Keithley 6430, Cleveland, OH).

Fig. 1 shows the XRD pattern of the BFZO thin film deposited on the $SrRuO_3/SrTiO_3(1\,1\,1)$ substrate. The film has a pure phase, and no secondary phases were detected except for these peaks of the substrate. Moreover, the (1 1 1) orientation was induced for the BFO thin film, owing to the induced growth of the $SrRuO_3/SrTiO_3(1\,1\,1)$ substrate.

Fig. 2(a) plots the dielectric constant ($\varepsilon_r$) and dielectric loss (tan$\delta$) of BFO and BFZO thin films, measured at the frequency of $10^0$–$10^6$ Hz and at room temperature. The $\varepsilon_r$ value of the BFZO thin film is higher than that of the BFO thin film, owing to the introduction of Zn [19]. Moreover, a lower tan $\delta$ value is demonstrated for the BFZO thin film as compared with that of the BFO thin film, owing to the involvement of a lower charge defects concentration, as confirmed by the leakage current density in Fig. 2(b). Fig. 2(b) shows the leakage current density vs applied electric field for the BFO and BFZO thin films, measured at room temperature. The BFZO thin film has a lower leakage current density than that of the BFO thin film, confirming the involvement of a low charge defect concentration in BFZO. The formation of defect complexes between $(Zn^{2+}_{Fe^{3+}})'$ and $(V_{O^{2-}})^{\bullet\bullet}$ may result in a lower leakage current density for the BFZO thin film, and similar phenomenon has been observed elsewhere [20]. The employment of a single crystal substrate and the Zn substitution should largely contribute to the decrease in the leakage current density of the BFZO thin film.

Fig. 3 shows the *M–H* curves of BFO and BFZO thin films, measured at room temperature. The introduction of Zn affects the saturation magnetizations ($M_s$) value of BFO thin films, that is, the

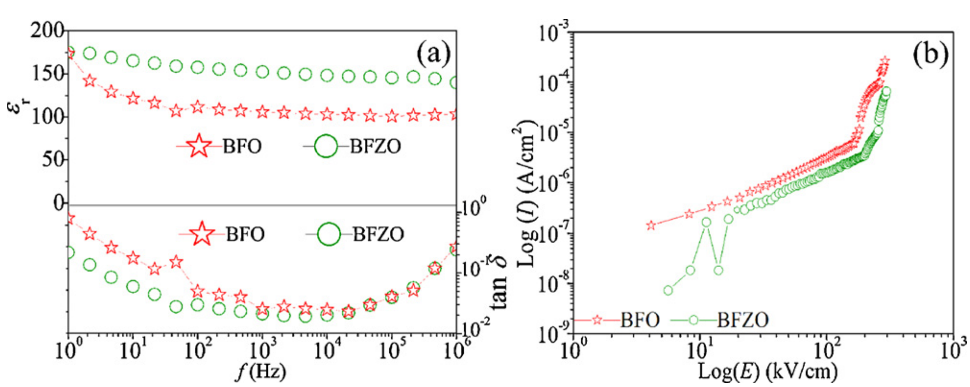


**Fig. 2.** (a) Dielectric properties and (b) log(*I*) vs *E* curves for the BFO and BFZO thin films.

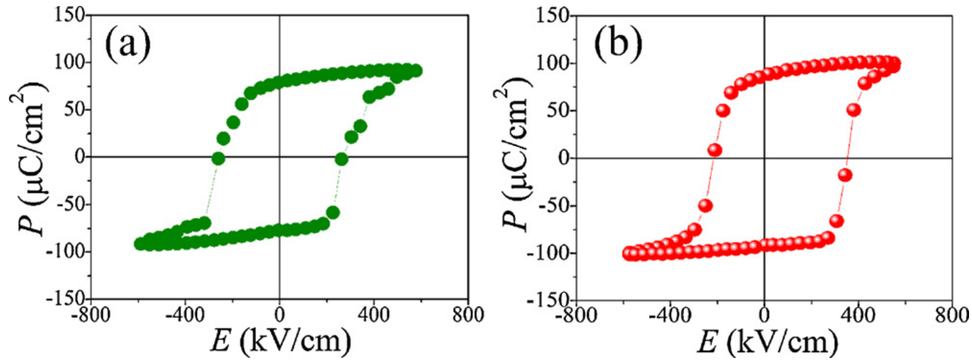


**Fig. 5.** *P–E* loops for (a) the BFZO thin film deposited on the $SrRuO_3/SrTiO_3$(1 0 0) substrate, and (b) the BFO thin film deposited on the $SrRuO_3/SrTiO_3$(1 1 1) substrate.

BFZO thin film has a lower $M_s$ value than that of the BFO thin film. The decrease in $M_s$ value can be attributed to the introduction of the nonmagnetic Zn composition [15,21]. The $Zn^{2+}$ substitution for $Fe^{3+}$ can suppress the formation of $Fe^{2+}$, and generates more oxygen vacancies in BFO [20]. Therefore, the $Fe^{2+}$ cannot contribute to the improvement of magnetic properties of BFO thin films [22].

Fig. 4 shows the *P–E* loops of the BFZO thin film deposited on the $SrRuO_3/SrTiO_3$(1 1 1) substrate, measured at 5 kHz and room temperature. A saturated *P–E* loop is observed for such a thin film. The insert in Fig. 4 plots the $2P_r$ and $2E_c$ values of the BFZO thin film as a function of applied electrical fields. At $E > \sim 250$ kV/cm, the remanent polarization slightly changes with an increase in applied electric fields, indicating that the BFZO thin film almost reaches a saturation. The *P–E* measurement cannot completely exclude the effect of the leakage current, and the pulsed polarization positive up negative down (PUND) measurement is performed at a pulse width of 0.2 ms and room temperature for accurately representing the polarization behavior and excluding the contribution of the leakage current towards the polarization, as shown in the insert in Fig. 4. The switchable polarization obtained by the PUND measurement is a little smaller as compared to that obtained from the *P–E* measurement, confirming that the leakage current density only plays a smaller role in affecting the ferroelectric behavior for the BFZO thin film deposited on the $SrRuO_3/SrTiO_3$(1 1 1) substrate. The BFZO thin film has a giant $2P_r$ value of $\sim$268.5 μC/cm$^2$ when measured at room temperature, which is superior to those of pure BFO thin films with (1 1 1) and other orientations [3,8–17], and is also much larger than that ($2P_r \sim 180.8$ μC/cm$^2$) of the BFO thin film deposited on the $SrRuO_3/SrTiO_3$(1 1 1) substrate in this work [Fig. 5(b)]. The crystal structure [18], the site engineering [14–17], and the orientation [3,8–10] usually contribute to the improvement in the polarization of BFO thin films. In the present work, the (1 1 1) orientation should largely contribute to the improvement in the polarization value for the BFZO thin film, where the largest spontaneous polarization occurs in the (1 1 1) direction because the ions are displaced along [1 1 1] directions from their equilibrium positions [23]. The site engineering further enhances the ferroelectric behavior of the BFZO thin film, where a large remanent polarization of $2P_r \sim 146$ μC/cm$^2$ has been exhibited for the Zn -modified BFO thin film with a polycrystal structure when measured at a low temperature of 80 K [15]. Moreover, a giant polarization value of the BFZO thin film is also induced by the low leakage current density caused by using the $SrTiO_3$ single crystal substrate and the introduction of Zn. Moreover, according to $\sqrt{3}P(1\,0\,0) = P(1\,1\,1)$ for the pure BFO thin film [8], the polarization value for (1 1 1) is also equal to be $\sqrt{3}P(1\,0\,0)$ for the BFZO thin film in this work, where the $2P_r$ value is about 160.6 μC/cm$^2$ for the BFZO thin film deposited on the $SrRuO_3/SrTiO_3$(1 0 0) substrate, as shown in Fig. 5(a). Therefore, the orientation, the site engineering, and the single crystal substrate contribute to the giant remanent polarization of the BFZO thin film in the present work.

In summary, the $BiFe_{0.96}Zn_{0.04}O_3$ thin film was fabricated on the $SrRuO_3/SrTiO_3$(1 1 1) substrate by rf sputtering, and a (1 1 1) orientation is induced due to the induced growth of the $SrRuO_{3/}SrTiO_3$(1 1 1) substrate. A better dielectric behavior is demonstrated for this film, while the magnetic properties of BFZO thin films are degraded by the introduction of nonmagnetic Zn compoistion. The (1 1 1) orientation, the Zn substitution, and a low leakage current density totally result in a giant polarization value of $2P_r \sim 268.5$ μC/cm$^2$ for the $BiFe_{0.96}Zn_{0.04}O_3$ thin film. Therefore, it is a promising approach to further improve the polarization value of bismuth ferrite thin films by the mixed tools of the site engineering, the single crystal substrate, and the orientation modification.

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