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A Method to Improve Electrical Properties of $BiFeO_3$ Thin Films

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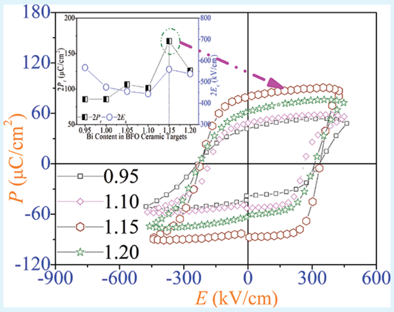
ABSTRACT: A method is used to improve the electrical properties of $BiFeO_3$ thin films by modifying the Bi content in ceramic targets, where all thin films were prepared on $SrRuO_3/Pt/TiO_2/SiO_2/Si(100)$ substrates by radio frequency sputtering. The Bi content in the ceramic target strongly affects the electrical properties of $BiFeO_3$ thin films. $BiFeO_3$ thin films prepared by using the ceramic target of Bi/Fe ≈ 1.15 with a molar ratio demonstrate a low leakage current density and a low dielectric loss. Moreover, a larger remanent polarization of $2P_r \approx 167.6\ \mu C/cm^2$ is also demonstrated for the $BiFeO_3$ thin films prepared by using the ceramic target of Bi/Fe ≈ 1.15, together with an improved fatigue behavior. Therefore, it is an effective way to improve the electrical properties of bismuth ferrite thin films by modifying the Bi content in ceramic targets.



KEYWORDS: *bismuth ferrite, bismuth content, electrical properties*

Multiferroic materials have received considerable attention because of the coexistence of ferroelectricity, (anti)-ferromagnetism, and ferroelasticity.[1−8] Among those, $BiFeO_3$ (BFO) lead-free multiferroic material demonstrates some promising and potential applications in the field of multifunctional devices, solar energy devices, ferroelectric random access memory, spintronics, and several other technologically demanding applications because of its giant remanent polarization of $P_r \approx 100\ \mu C/cm^2$,[2,9−11] a high Curie temperature of $T_c \approx 1104$ K,[3−5] the coexistence of ferroelectricity and antiferromagnetism,[3,4] and environmental friendliness.[2−11] In contrast, a large leakage current density at room temperature seriously hinders the practical application of BFO.[12,15]

Several methods have been conducted to improve the electrical properties of BFO thin films by reducing its leakage current density,[2,9,11,14−27] for example, the use of a single-crystal substrate,[2,9,11,14] the employment of an oxide buffer layer,[16−18] the use of site engineering,[14,19−21] the construction of a multilayer structure,[22,23] and control of the deposition parameters.[24−27] Among those attempts, some deposition parameters (i.e., oxygen partial pressure, kinetic growth parameters, and deposition temperature) are very promising tools to not only reduce leakage current but also improve the multiferroic properties of BFO thin films.[24−27] For example, enhanced ferroelectric properties have been demonstrated in BFO thin films by choosing an optimum deposition temperature during sputtering.[24,25] The oxygen content during radio frequency (rf) sputtering has affected the leakage current density and multiferroic behavior of BFO thin films with a sintering aid of CuO, and a larger remanent polarization has been induced by optimizing the oxygen content.[27] It is believed that the loss of Bi is partly responsible for a high leakage current density in BFO thin films,[12−15] $2Bi^{3+} + 3O^{2-} \rightarrow Bi_2O_3(\text{evaporation}) + 2V_{Bi}^{3-} + 3V_O^{2+}$. As shown in the above equation, if Bi^{3+} ions volatilize in BFO, oxygen vacancies (V_O^{2+}) and bismuth vacancies (V_{Bi}^{3-}) will be generated, resulting in a higher conduction of BFO-based materials.[12−15] Therefore, it becomes critical to control or modify the bismuth content of BFO thin films during the preparation of ceramic targets and the deposition of BFO thin films by using rf sputtering. Although the rf sputtering has been successfully demonstrated for the deposition of BFO thin films,[11] it is difficult for rf sputtering to control the chemical composition of deposited thin films. Except for the oxygen content and the deposition temperature during rf sputtering, the chemical composition of ceramic targets may be also beneficial to the electrical properties of BFO thin films. Moreover, there are few systematical reports on the effect of the Bi content in ceramic targets on the electrical properties of BFO thin films prepared by rf sputtering.

In this letter, a method is used to enhance the electrical properties of BFO thin films by tailoring the Bi content in ceramic targets, and BFO thin films have been prepared on $SrRuO_3(SRO)/Pt/TiO_2/SiO_2/Si(100)$ substrates by rf sputtering. The effects of the Bi content in ceramic targets on the electrical properties of BFO thin films were mainly investigated. An enhanced remanent polarization and an improved fatigue behavior are also demonstrated in BFO thin films prepared by using the ceramic target of Bi/Fe ≈ 1.15, together with a low leakage current density. As a result, it is an effective way to improve the electrical properties of bismuth ferrite thin films by modifying the Bi content in ceramic targets.

Two-inch Bi_xFeO_3 (x = 0.95, 1.00, 1.05, 1.10, 1.15, and 1.20) ceramic targets were synthesized by a solid-state reaction of constituent oxides, namely Bi_2O_3 and Fe_2O_3. Powder mixtures of these oxides were calcined at ~750 °C in air for 6 h to form these phases, and then these green bodies were sintered at ~830 °C for 2 h to form these polycrystalline ceramic targets.

Received: February 10, 2012
Accepted: March 12, 2012
Published: March 14, 2012

dx.doi.org/10.1021/am300236j | *ACS Appl. Mater. Interfaces* 2012, 4, 1182−1185

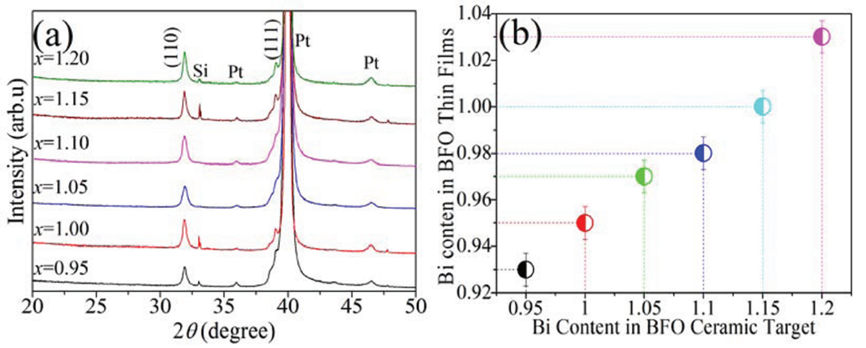


Figure 1. (a) XRD patterns of BFO thin films with the ceramic targets of different Bi content, and (b) Bi content of BFO thin films as a function of Bi content in ceramic targets.

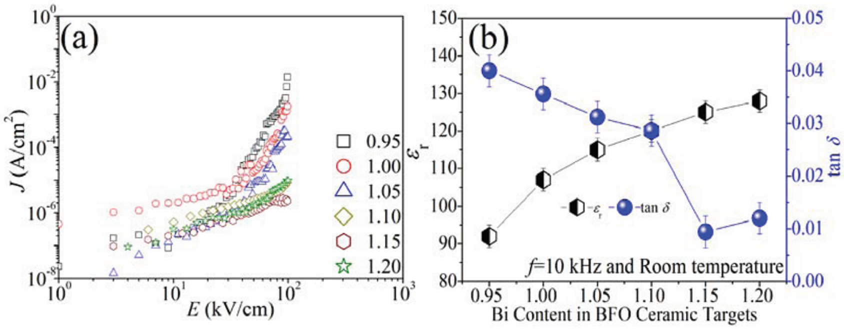


Figure 2. (a) J–E curves and (b) dielectric behavior of BFO thin films as a function of Bi content in ceramic targets.

$BiFeO_3$ thin films were deposited by rf sputtering from Bi_xFeO_3 ceramic targets, and $BiFeO_3$ thin films with a fixed thickness of ~250 nm were deposited on $SRO/Pt/TiO_2/SiO_2/Si(100)$ substrates at the same substrate temperature of ~570 °C. $BiFeO_3$ thin films were deposited at a rf power of ~120 W, and the rf deposition was carried out at a base pressure of $\sim 3.0 \times 10^{-6}$ Torr and a deposition pressure of 10 mTorr with Ar and O_2 at the ratio of 4:1. The SRO buffer layer was deposited by rf sputtering at the same substrate temperature of ~650 °C under a rf power of 80 W, and the rf deposition was carried out under a base pressure of 3.0×10^{-6} Torr and a deposition pressure of 10 mTorr with Ar and O_2 at a ratio of 4:1. Circular Au electrodes of diameter 0.20 mm were sputtered on the film's surface using a shadow mask in order to investigate their electrical properties.

The phase structure of thin films was analyzed by using the X-ray diffraction (XRD) (Bruker D8 Advanced XRD, Bruker AXS Inc., Madison, WI, CuKa). Ferroelectric properties of thin films were studied by using the Radiant precise workstation (Radiant Technologies, Medina, NY). The leakage current density of thin films was measured by using a Keithley meter (Keithley 6430, Cleveland, OH).

Figure 1a shows the XRD patterns of BFO thin films prepared by using the ceramic targets with different Bi content. All thin films appear to be pure phase in the measurement range of XRD. Moreover, the mixture of (110) and (111) orientations is demonstrated for all BFO thin films regardless of the Bi content in ceramic targets. The Bi content in BFO thin films as a function of the Bi content in ceramic targets is shown in Figure 1b. The Bi concentration of BFO thin films is obviously different from those in ceramic targets, that is, the Bi content of BFO thin films is lower than those of ceramic targets, giving for example a BFO thin film with $x \approx 1.00$ from a BFO ceramic target with $x \approx 1.15$. The large difference in the Bi content between BFO thin films and ceramic targets should be attributed to the loss of bismuth during the preparation in ceramic targets and the deposition in thin films.

Figure 2(a) shows the J–E curves of BFO thin films prepared by using the ceramic target of different Bi/Fe ratios. BFO thin films prepared by using the ceramic target of Bi/Fe < 1.15 have a much higher leakage current density than those of thin films prepared by using the ceramic target of Bi/Fe ≥ 1.15. The loss of Bi often results in the generation of more oxygen and bismuth vacancies in BFO thin films,[12−15] and the equation of the defect chemistry for BFO is listed below: $2\ Bi^{3+} + 3O^{2-} \rightarrow Bi_2O_3$ (volatization) + $2V_{Bi}^{3-}$ + $3V_O^{2+}$. Therefore, a higher leakage current density of BFO thin films prepared by using the ceramic target of Bi/Fe < 1.15 could be attributed to the involvement of more V_{Bi}^{3-} and $3V_O^{2+}$. Figure 2b shows the dielectric behavior of BFO thin films as a function of Bi content in ceramic targets, measured at f = 10 kHz and room temperature. The dielectric constant (ε_r) of BFO thin films gradually increases with an increase in the Bi content of ceramic targets because of the involvement of different conductivity.[28] Moreover, BFO thin films prepared by using the ceramic target of Bi/Fe < 1.15 demonstrate a higher dielectric loss (tan δ) as compared with those of thin films prepared by using the ceramic target of Bi/Fe ≥ 1.15, which is well in agreement with the change of the leakage current density in Figure 2a. The low tan δ value confirms the involvement of a low defect charge in BFO thin films prepared by using the ceramic target of Bi/Fe = 1.15.

Figure 3a shows the P–E hysteresis loops for the BFO thin films as a function of Bi content in ceramic targets, measured at 5 kHz and room temperature. Similarity to the change of J–E curves, a better P–E loop with a larger remanent polarization (P_r) is demonstrated in the BFO thin film prepared by using the ceramic target of Bi/Fe = 1.15, whereas a nonsaturated and

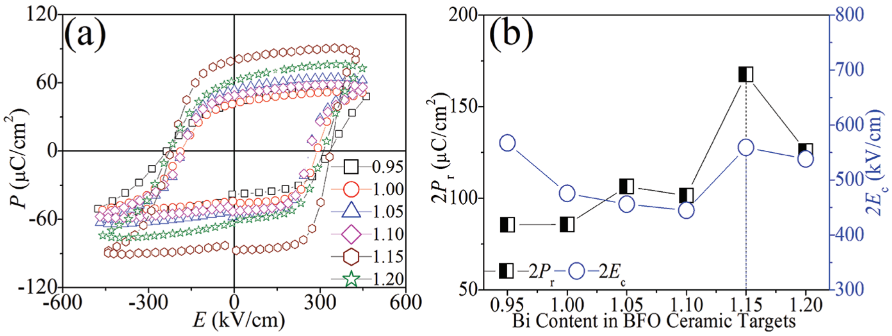


Figure 3. (a) P–E curves and (b) $2P_r$ and $2E_c$ values of BFO thin films as a function of Bi content in BFO ceramic targets.

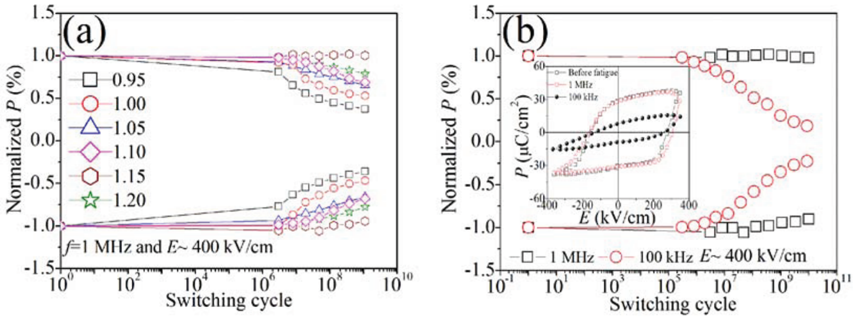


Figure 4. (a) Fatigue behavior of BFO thin films as a function of Bi content in BFO ceramic targets, and (b) fatigue behavior of BFO thin films prepared by using the ceramic target of Bi/Fe = 1.15 as a function of measurement frequency, where the inset in b is P–E loops before and after fatigue for such a thin film in b.

a low remanent polarization are observed for BFO thin films prepared by using the ceramic target of Bi/Fe < 1.15 and Bi/Fe > 1.15, as shown in Figure 3a. A $2P_r$ value of ~167.6 μC/cm^2 is demonstrated in the BFO thin film prepared by using the ceramic target of Bi/Fe = 1.15, which is larger than those of BFO thin films reported by other authors,[2,14,16,17,19,22,23] as shown in Figure 3b. Several factors could be responsible for the improvement in the ferroelectric properties of BFO thin films in this work. First, a low leakage current density, which by compensating the loss of Bi is largely responsible for the improved ferroelectric properties of bismuth ferrite thin films.[12−15] Second, the mixture of (110) and (111) orientations also improves the ferroelectric properties of BFO thin films, where the [111] is the polar axis for the BFO materials.[9−11]

Figure 4a plots the fatigue behavior of BFO thin films as a function of Bi content in ceramic targets, measured at f = 1 MHz and the driven electric field of ~400 kV/cm. The BFO thin film prepared by using the ceramic target of Bi/Fe=1.15 has a better fatigue behavior than those of thin films prepared by using the ceramic target of Bi/Fe < 1.15 and Bi/Fe > 1.15, where there is almost no change in the polarization value after a switching cycle of ~1 × 10^9. Moreover, the fatigue behavior of BFO thin films is improved with the increase of Bi/Fe ratio, owing to the decrease in oxygen vacancies.[29,30] Figure 4b plots the frequency dependence of the fatigue behavior of BFO thin films prepared by using the ceramic target of Bi/Fe = 1.15 driven by triangular bipolar pulses under a fixed driving field of ~400 kV/cm. The fatigue behavior is deteriorated with a decrease in measurement frequencies from 1 MHz to 100 kHz. When fatigued at a high frequency of 1 MHz, this film is fatigue-free at the switching cycle of ~9.86 × 10^9. However, the fatigue endurance of this film gradually decreases with increasing the switching cycles when fatigued at a low frequency of 100 kHz, and the polarization value is lowered by ~23% from the initial value upon ~9.86 × 10^9 switching cycles. P–E loops in the insert of Figure 4b confirm the change of the fatigue endurance of BFO thin films prepared by using the ceramic target of Bi/Fe = 1.15 as a function of measurement frequencies. Some explanations have been used to illuminate this phenomenon: when fatigued at a high fatigue frequency, oxygen vacancies and deep traps in a film respond slowly to the driving field, and the compensation of polarization charges is performed mainly with free carriers from the top and bottom electrodes.[31] As a result, the polarization value does not change dramatically. However, oxygen vacancies can migrate easily and trapped charges respond steadily to the driving field when fatigued at a low fatigue frequency. The rearrangement of oxygen vacancies blocks the switching of ferroelectric domain, leading to a dramatic decrease in polarization.[29−31] Therefore, the low fatigue frequency results in the degradation of fatigue behavior of this film.

In conclusion, a method is used to effectively enhance the electrical properties of $BiFeO_3$ thin films by tailoring the Bi content in ceramic targets, and $BiFeO_3$ thin films were prepared on $SrRuO_3/Pt/TiO_2/SiO_2/Si(100)$ substrates by radio frequency sputtering. Effects of Bi content in ceramic targets on the electrical properties of $BiFeO_3$ thin films have been investigated. A low leakage current density and a low dielectric loss are induced for the $BiFeO_3$ thin film prepared by using the ceramic target of Bi/Fe = 1.15. Moreover, such a $BiFeO_3$ thin film also demonstrates a larger remanent polarization and an improved fatigue behavior. Therefore, it is an effective way to improve the electrical properties of bismuth ferrite thin films by modifying the Bi content in ceramic targets.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Dr. Jiagang Wu gratefully acknowledges the supports of the National Natural Science Foundation of China (51102173), the introduction of talent start funds of Sichuan University (2082204144033), and the National University of Singapore.

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