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Preparation and Properties of Composite Films with Different Layer Ratios

Jiahua Wei*, Wenlong Liu

School of Electronic Information and Artificial Intelligence, Shaanxi University of Science and Technology, Xi'an, 710021, China
**Corresponding authors: jehu1228218064@163.com*

Abstract: *In the field of multifunctional electronic components, the multiferroic material $BiFeO_3$ which exhibits both ferroelectricity and ferromagnetism at room temperature, has become a research hotspot. In this study, the sol-gel method was employed to prepare $Bi_{0.89}Tb_{0.11}Fe_{0.96}Mn_{0.02}Co_{0.02}O_3/ZnFe_2O_4$ (BTFMCO/ZFO) bilayer films with different layer ratios on FTO substrates, and the effects of different layer ratios on the ferroelectric and ferromagnetic properties of the films were investigated. The change in different layer ratios can cause significant variations in the relative intensities of the diffraction peaks of the BFO phase and the ZFO phase, which can be attributed to the stress-strain effect caused by the mismatched lattice layers between the two phases. Through a comprehensive evaluation of the leakage current, dielectric constant, and ferroelectric properties of five groups of composite films, we found that the BTFMCO-ZFO composite film with a layer ratio of 12/1 exhibits the most excellent electrical performance.*

Keywords: *$BiFeO_3$, Thin films, Ferroelectricity, Ferromagnetism, Sol-gel*

1. Introduction

Among the many multiferroic materials, $BiFeO_3$ (BFO) thin films have attracted significant attention due to their unique room-temperature ferroelectric and ferromagnetic properties, demonstrating potential value in the development of new types of multifunctional electronic devices[1,2]. Nevertheless, the practical application of pure BFO thin films faces numerous challenges, including oxygen vacancies caused by the volatilization of Bi^{3+} ions, valence fluctuations of Fe^{3+} ions, and the substantial leakage current they induce, as well as their inherently weak ferromagnetism. These issues limit the full expression of performance and the scope of application for BFO thin films[3–5].

In this study, in order to enhance the multiferroicity of the thin film, we chose to dope the Tb element at the A-site of the BFO thin film, and co-dope the B-site with Mn and Co elements to form a Tb, Mn, and Co co-doped $Bi_{0.89}Tb_{0.11}Fe_{0.96}Mn_{0.02}Co_{0.02}O_3$ thin film. We also used the $ZnFe_2O_4$ (ZFO) thin film to construct a molecular layer composite film and prepared composite films with different layer ratios. Based on this, the $Bi_{0.89}Tb_{0.11}Fe_{0.96}Mn_{0.02}Co_{0.02}O_3/ZnFe_2O_4$ (BTFMCO/ZFO; layer ratios: 12/1,12/2, 14/1,14/2, 12/4) bilayer films were prepared on the FTO/glass substrate by the sol-gel method. The effects of different layer ratios on the structure, leakage current, dielectric properties, and multiferroic characteristics of the bilayer films were investigated.

2. Experiment

$Bi_{0.89}Tb_{0.11}Fe_{0.96}Mn_{0.02}Co_{0.02}O_3/ZnFe_2O_4$ (BTFMCO/ZFO, layer ratios: 12/1, 12/2, 14/1, 14/2, 12/4) bilayer films were prepared on FTO/glass substrates by the sol-gel method. Firstly, $Bi(NO_3)_3·5H_2O$, $Tb(NO_3)_3·6H_2O$, $Fe(NO_3)_3·9H_2O$, $C_4H_6MnO_4·4H_2O$ and $Co(NO_3)_2·6H_2O$ and $C_4H_6O_4Zn_4·H_2O$ were dissolved in a mixture of $CH_3OCH_2CH_2OH$ and $C_4H_6O_3$ according to the molar ratio, and then stirred to obtain the BTFMCO and ZF0 precursor solutions (0.2 mol/L). Secondly, the ZFO precursor solution was spin-coated onto the FTO/glass substrate, and then, using the same spin-coating method, the BTFMCO layer was prepared cyclically, and the corresponding number of cycles was carried out according to different layer ratios. Finally, a gold top electrode with an area of 0.125 mm² was sputtered onto the surface of the film, and then the film was annealed at 285 °C for 20 minutes.

The structure of the thin films is examined using an X-ray diffractometer (XRD, A-D/max-2200. The electric hysteresis loops (P-E loops) of the films were measured by a Radiant Precision Multiferroic. Agilent B2901A was used to measure the leakage current density of the thin films.

3. Results and discussion

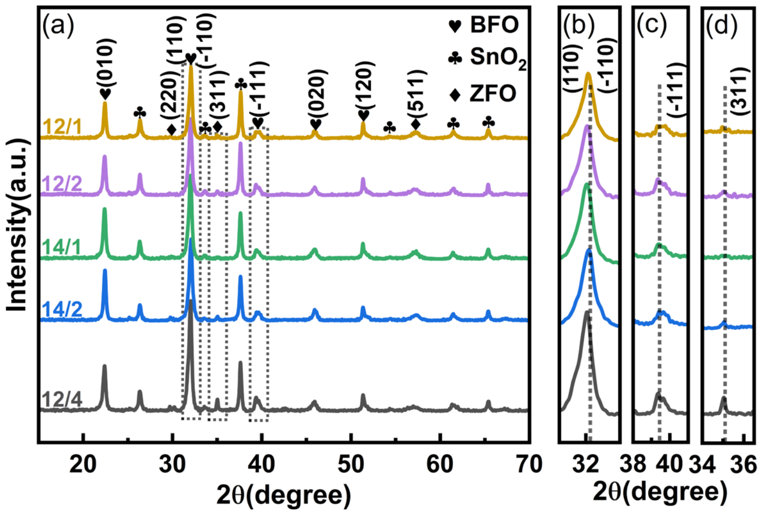

Fig. 1 (a) the XRD pattern; (b) the enlarged view at 2θ = 31.5° - 32.7°; (c) the enlarged view at 2θ = 38°- 41°; (d) the enlarged view at 2θ = 34° - 36.5° of BTFMCO-ZFO composite thin films

Figure 1(a) shows the XRD patterns of BTFMCO-ZFO composite films with different layer ratios (12/1, 12/2, 14/1, 14/2, 12/4). Among them, the BTFMCO layer matches the PDF standard card (JCPDS No.: 72-2112), exhibiting the characteristics of a rhombohedral distorted perovskite heterostructure representing the R3m space group; while the ZFO layer is consistent with the PDF standard card (JCPDS No.: 73-1963), with a cubic crystal structure belonging to the Fd-3m space group. In the XRD patterns, except for the diffraction peaks corresponding to the target product and the SnO_2 substrate, no other impurity peaks were detected. This indicates that the prepared composite film samples contain no intermediate compounds, and the composite films have extremely high crystallinity, characterized by the coexistence of the BTFMCO phase and the ZFO phase. Compared with the XRD pattern of the classical pure-phase BFO film, the pattern in this study significantly differs in that the two diffraction peaks in the [110] and [-110] directions overlap and show a trend of a single peak. This is most likely due to the ternary co-doping effect of (Tb, Mn, Co), which leads to a slight structural transformation of the BFO layer.

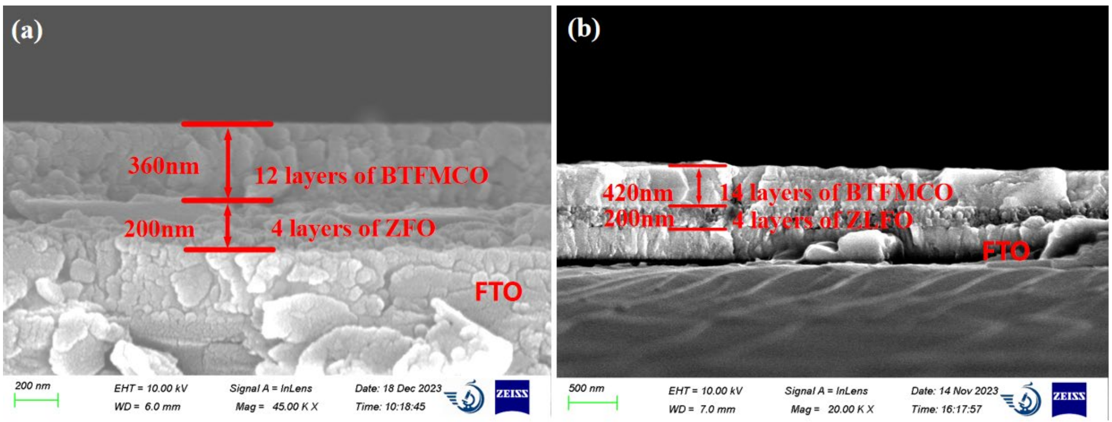

Fig. 2 BTFMCO-ZFO cross-section morphology for 12/4 layer ratio

Figure 2 shows the cross-sectional SEM image of the BTFMCO-ZFO composite film with a 12/4 layer ratio. It can be clearly distinguished from the figure that the composite film presents a clear three-layer layered structure, with 12 layers of BTFMCO, 4 layers of ZFO and FTO layers from top to bottom. Among them, the interface between the BTFMCO layer and the ZFO layer is clearly identifiable, and no obvious signs of diffusion reaction are observed at the interface, which indicates that there is good interfacial stability and independence between the two layers. Measured by the electronic ruler, the

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thickness of the 12 layers of BTFMCO is about 360nm, and the thickness of the 4 layers of ZFO is about 200nm.

Figure 3 shows the leakage current curves of BTFMCO-ZFO composite films with different layer ratios (12/1, 12/2, 14/1, 14/2, 12/4). It can be seen from the figure that the change of different layer ratios has a relatively weak effect on the leakage current of the composite film. Among them, the leakage current density exhibited by the BTFMCO-ZFO composite film with a layer ratio of 12/1 is relatively lower than that of the other layers than the composite film. This phenomenon may be due to the reduction of the film thickness and the relative reduction of its internal defects.

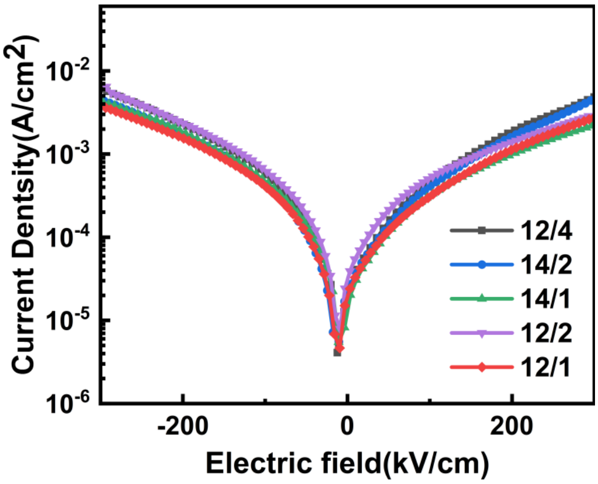

Fig. 3 Leakage current density of BTFMCO-ZFO composite films with different layer ratios.

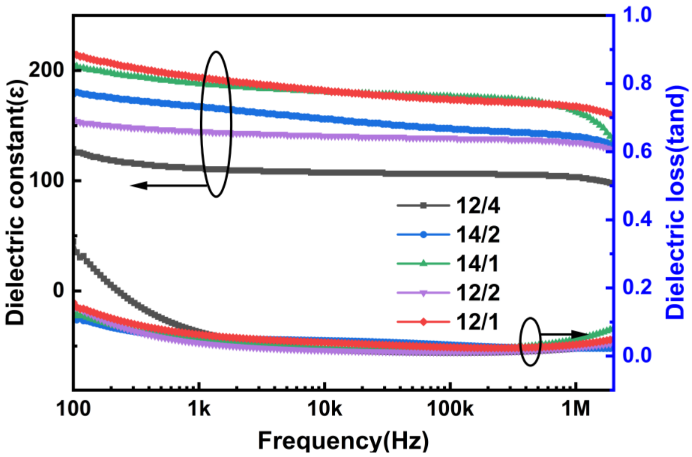

Fig. 4 Dielectric constant (εr) and dielectric loss (tanδ) of BTFMCO-ZFO composite films with different layer ratios

Figure 4 shows the dependence of the room temperature dielectric constant (ε_r) and dielectric loss (tan δ) of different layer ratios of BTFMCO-ZFO composite films (12/1, 12/2, 14/1, 14/2, 12/4) with frequency, covering the test frequency range from 100Hz to 2MHz.All composite films exhibited low dielectric loss levels over the entire test frequency range, with relatively high dielectric losses at lower frequencies (below 1 kHz), mainly due to the Maxwell-Wangner interface polarization effect and space charge polarization . The dielectric constants of all composite films showed a downward trend with increasing frequency, mainly due to the fact that some dipoles (such as space charges) could not keep up with changes in the frequency of the applied electric field, which in turn reduced their contribution to film polarization .

Fig. 5 presents the hysteresis loops of BTFMCO-ZFO composite films with different layer ratios (12/1, 12/2, 14/1, 14/2, 12/4) at room temperature and at the test frequency of an applied electric field at 1 kHz. The observation results show that among the five groups of composite films tested, the composite films with a layer ratio of 12/1 exhibit the optimal ferroelectric properties. The difference in ferroelectric properties is inferred to be related to the distribution of stress and strain between the layers of the composite films, which are caused by different layer ratios.

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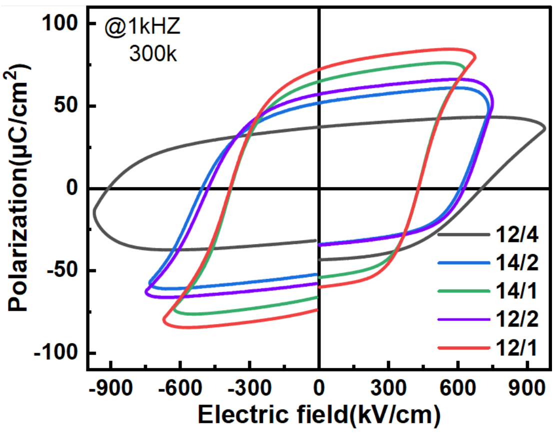

Fig. 5 Electric hysteresis loops (P–E) of BTFMCO-ZFO composite films with different layer ratios

4. Conclusion

BTFMCO/ZFO composite films with different layer ratios (12/1, 12/2, 14/1, 14/2, 12/4) were successfully prepared on FTO/glass substrates by the sol-gel method. The XRD results show that the change in different layer ratios can cause significant variations in the relative intensities of the diffraction peaks of the BFO phase and the ZFO phase. This change is mainly attributed to the stress-strain effect caused by the mismatched lattice parameters between the BTFMCO layer and the ZFO layer when they are combined. Through a comprehensive evaluation of the leakage current, dielectric constant, and ferroelectric properties of five groups of composite films, we found that the BTFMCO-ZFO composite film with a layer ratio of 12/1 exhibits the most excellent electrical performance.

Acknowledgements

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Conflict of Interest

The authors have no conflicts to disclose.

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