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Ferroelectric and Electrical Properties Optimization of Mg-doped BiFeO₃ Flexible Multiferroic Films

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Abstract: Bi₃₋ₓMgₓFeO₃ (BMFO, x = 0, 0.02, 0.04, 0.06 and 0.08) multiferroic films were directly synthesized on flexible stainless steel (FSS), save the bottom electrode process, by means of sol–gel spin-coating technology. The effects of different bending conditions on ferroelectric, dielectric and leakage-current properties of BMFO films were investigated. The leakage-current densities of BiFeO₃ (BFO, x = 0) and BMFO (x = 0.06) films were 5.86 × 10⁻⁴ and 3.73 × 10⁻⁷ A/cm², which shows that the BMFO (x = 0.06) has more than three orders of magnitude lower than that of BFO film. The residual polarization (2 Pr) can be enhanced from 120 to 140 μC/cm². The proper doping of Mg in BiFeO₃ film could provide an effective method for reducing the leakage-current values as well as boosting the ferroelectric properties. In this study, the leakage-current mechanism of low electric field and high electric field of BMFO film is analyzed and established. In addition, the flexible BMFO film maintains practical ferroelectric and leakage-current properties at retention time of 10⁶ s under different symmetry bending conditions. These results indicate that the BFMO film will be very practical in opto-electronic and storage device applications.

Keywords: multiferroic films; flexible; ferroelectric; polarization; leakage current; retention

1. Introduction

Nowadays, many new technologies in science have created amazing and rapid development in the miniaturization of devices, and electronic products have made humans an important driving force for the quality of life. The rise of flexible electronic products, with excellent flexibility, portability and lightness, is currently actively entering the electronics market [1–4]. Considering ergonomics to make it easier for users to carry, when the appearance of electronic products begins to bend, the structure and various characteristics and functions of the internal components will also change accordingly. Therefore, the current electronic products on the market are gradually becoming flexible, which has led many researchers to invest in flexible film research [5–7].

Ferroelectric materials not only have more superior characteristics in memory element applications, but also have a wide range of applications including sensors, actuators, piezoelectrics, spin electrons and microelectronic devices. There are many kinds of ferroelectric materials can be used for thin films devices, among which Pb(Zr, Ti), O₃ (PZT), SrBi₂Ta₂O₉ (SBT), BaTiO₃, BFO, etc. However, nonartificial materials that have both ferroelectric and ferromagnetic properties are rarer. Among these materials, BFO is the only ferroelectric and antiferromagnetic properties that coexist at room temperature multiferroic materials, and the BFO Curie temperature (1123 K) and Néel temperature (653 K) are higher than other ferroelectric materials [8–10]. However, BFO film usually has a high leakage-current density due to the oxygen vacancy and the state of iron ions (Fe³⁺ to Fe²⁺ state)
resulting from various oxygenations. This is a critical barrier hindering the development of practical application. Therefore, many efforts have been made to reduce the leakage-current density. Recently, the performance of BFO films could be improved by optimizing the process parameters and ion doping technique [11–17]. Compared with the process technology, ion doping has some advantages such as convenient operation, easy to realize the microstructure and characteristics of the film. Therefore, it has been widely used in the synthesis of high-quality BFO-based films. On the basis of current results chemical substitution is one of the most useful methods. Among them, the most popular substitution ions are the rare earth elements [18–21].

In this study, a Sol–Gel method was applied to grow BFO-doped Mg films on flexible stainless steel (FSS) substrate. The microstructure, ferroelectric, leakage current and dielectric properties in different bending conditions of BMFO flexible nanocrystalline films with different magnesium doping amounts were discussed.

2. Materials and Methods

The popular chemical formulas of the precursor solutions of $\text{Bi}_{1-x}\text{Mg}_x\text{FeO}_3$ (BMFO, $x = 0, 0.02, 0.04, 0.06$ and $0.08$) were composed of Bismuth acetate ($\text{Bi(OOCCH}_3)_3$, Alfa, 99.99% purity), magnesium acetate ($\text{Mg(OOCCH}_3)_2\cdot\text{xH}_2\text{O}$, Alfa, 99.9% purity), manganese acetate ($\text{Mn(C}_2\text{H}_3\text{O}_2)_2\cdot\text{4H}_2\text{O}$) and iron acetylacetonate ($\text{Fe(CH}_3\text{COCOCH}_3)_3$, Alfa, 99.9% purity) were used as source materials. Propionic acid and 2-methoxyethanol was used as solvents. A stock solution of $\sim 0.1$-M concentration was obtained by a sol–gel method. Use an inductively coupled plasma mass spectrometry (ICP-MS) instrument to confirm that the deviation from stoichiometry was within $\pm 1\%$.

The BMFO solution was directly spin-coated onto FSS substrate at a spin rate of 2500 rpm for 30 s. After each coating step, the gel films were pyrolyzed on a hot plate at $300$ °C for 2 min before final annealing. After multilayer coating, the BMFO films were annealed at $450$ °C, $500$ °C, $550$ °C and $600$ °C by rapid thermal annealing (RTA) in the ambient atmosphere at a heating rate of $100$ °C/min for 2 min. In this study, the BMFO films annealed at $500$ °C have the best ferroelectric properties and lowest leakage-current properties. Hereafter the analysis will be focused on the BMFO films (thickness 300 nm) annealed at $500$ °C.

The crystallization and microstructures of all BMFO films were determined by X-ray diffraction (XRD) patterns using a Rigaku PC-2200 X-ray diffractometer with CuKα radiation, which was operated at an accelerating voltage of $40$ kV and an emission current of $20$ mA. The XRD data were recorded at room temperature in the $2\theta$ range from $20^\circ$ to $60^\circ$ with a stepping width of $0.01^\circ$ and a scanning speed of $0.5^\circ$/min. The top silver electrodes with an area of $7.85 \times 10^{-3}$ cm$^2$ were prepared by thermal evaporator. The measurements of dielectric constant and loss tangent values were performed by using an Agilent 4284A impedance analyzer. Measurements of the ferroelectric hysteresis loops were carried out in a Sawyer-Tower circuit in a metal-ferroelectric-metal (MFM) configuration. The leakage-current density was measured using Keithley 2400 source meter with voltages varying from 0 to 5 V in a MFM configuration.

3. Results and Discussions

Figure 1 presents the XRD patterns measured from the BMFO ($x = 0, 0.02, 0.04, 0.06$ and $0.08$) films. The positions of these XRD peaks are quite similar to those of the standard diffraction pattern data of BFO collected in the JCPDS card. The pure BFO thin film shows a polycrystalline rhombohedral perovskite structure with the space group R3c. No obvious second phase was observed for all the samples, indicating that the Mg-substitution has a benefit for stabilizing the perovskite structure. The (110) and (104) diffraction peaks in the $2\theta$ ranges of $31^\circ$ to $33^\circ$ for the BFO films have a tendency to become a single peak by substituting Bi ions with Mg-doping. Close inspection of the (110) and (104) diffraction indicates an asymmetrical character of the reflection it means that at least two peaks may be resolved during fitting. The slight change in the angle may suggest for enhanced distortion of
the octahedron for the doped samples [22]. Meanwhile, when the amount of Mg-doping is too large, 
x = 0.08, it will cause a serious lattice structure distortion of the film.

Figure 1. XRD patterns of Bi$_{1-x}$Mg$_x$FeO$_3$ films with x = 0, 0.02, 0.04, 0.06 and 0.08. The * symbol in the
figure represents FSS.

The average grain sizes of BMFO films from the XRD peaks were calculated by using
Debye-Scherrer’s formula [23]: 

$$D = \frac{k \lambda}{\beta \cos \theta}$$

where D is the average grain size, k is a Scherrer constant (0.94), \(\lambda\) is wavelength of
the X-ray radiation (1.54 Å), \(\beta\) is the full width at half maximum, and \(\theta\) is the Bragg
diffraction angle. The average grain sizes of BMFO films are found to be about
31.93, 22.97, 21.57, 19.55 and 19.62 nm, for x = 0, 0.02, 0.04, 0.06 and 0.08, respectively. It is generally
known that the ion radius of Mg$^{2+}$ (0.72 Å) is much smaller than the Bi$^{3+}$ (1.03 Å). With an appropriate
increase of the Mg-doping amount, the lattice structure of the film changes, which results in greater
resistance to the film grain boundary migration. As a result, the grain growth rate is reduced, and the
grain size of the film is gradually smaller. The change of surface morphology of the film has a relative
impact on the change of crystal grain size caused by Mg-doping [24].

The ferroelectric hysteresis loops measured for the BMFO films at different applied electric fields
and at frequency 10 kHz are shown in Figure 2. The residues remnant polarization (2 Pr) and the
coercive field (2 Ec) of BMFO films for x = 0, 0.02, 0.04, 0.06 and 0.08 are 120, 124, 130, 140, 90 \(\mu\)C/cm$^2$ and
48, 40, 39.3, 38, 24 kV/cm$^2$, respectively. Enhanced 2 Pr and 2 Ec values of 140 \(\mu\)C/cm$^2$ and 38 kV/cm$^2$
were obtained for the BMFO film with x = 0.06, which shows the optimal amount of spontaneous
polarization for all the samples. The remanent polarization of Mg properly doped in BFO films are
found to be increases remarkably. It is proposed that doping with Mg ion led to improve the oxygen
ion stability in the lattice site of BFO and hence improve the fatigue resistance [25]. Due to some
Bi$^{3+}$ ions in the pseudo–perovskite layers containing Fe–O octahedral are substituted by Mg$^{2+}$ ions. Moreover, the substitution of Bi$^{3+}$ ions by Mg$^{2+}$ having smaller ionic radius than bismuth, maintain
a significant structural distortion of the perovskite structure of BFO, and improves the ferroelectric
properties resulting enhanced 2 Pr value [26].

Figure 3 is showing the leakage-current density (J) as a function of the electric field (E) for
the BMFO films. For the case of BMFO films, the leakage current increases with the increasing electric
field. Evidently, doping of Mg can reduce the leakage-current density of BMFO films. Among all
samples, BMFO (x = 0.06) film shows the lowest leakage-current density (3.73 \(\times\) 10$^{-7}$ A/cm$^2$), which
demonstrates a big improvement. A more than three orders reduction of leakage current compared
to that of BFO film (5.86 \(\times\) 10$^{-4}$ A/cm$^2$) was observed at applied field 50 kV/cm. The doping of Mg
effectively stabilizes the electrons hopping of Fe$^{3+}$ and Fe$^{2+}$, reduces the generation of oxygen vacancies,
and effectively improves the problem of high leakage current in BFO film. However, when the amount
of Mg-doping increases to x = 0.08, the film leakage-current density will increase. This phenomenon is
due to the amount of Mg-doping that causes the distortion of the Fe–O octahedron in BMFO film to
a critical point and cause leakage current to increase. Based on the results of surface morphologies analysis for BMFO films compared to the undoped ones, we found that the smaller grain size should be one of the main causes responsible for the lower leakage currents in the high-electric-field region.

![Ferroelectric hysteresis loops](image)

**Figure 2.** Ferroelectric hysteresis loops of Bi$_{1-x}$Mg$_x$FeO$_3$ (BMFO) films with (a) $x = 0$, (b) $x = 0.02$, (c) $x = 0.04$, (d) $x = 0.06$ and (e) $x = 0.08$.

![Leakage-current density](image)

**Figure 3.** Leakage-current density ($J$)–electric field ($E$) plots of BMFO films.

In this work, the dielectric constant ($\varepsilon_r$) began to appear stable when the frequency was higher than 510 kHz of the BMFO films. The $\varepsilon_r$ at 510 kHz for the BMFO ($x = 0.06$) film (55.29) was larger than that of BFO film (22.2). Throughout the test frequency, the dielectric constant of BMFO films was always greater than that of pure BFO film. This increase in dielectric constant value may be attributed to the decrease in the lone pair activity of the Bi$^{3+}$ after the gradual addition of higher amounts of Mg$^{2+}$ ions to BFO which is responsible for the ferroelectric distortion and dipolar polarization those contribute towards enhancing the dielectric constant. Meanwhile, the enhancement in the dielectric constant for BMFO films may be due to the suppression of impurity phases and microstructure oxygen vacancies.
vacancies (V_{O_2}^+) by the doping of Mg^{2+} ions for volatile Bi^{3+}. The dielectric loss (tan δ) at 510 kHz for the BMFO films (0.051) was smaller than that of the pure BFO film (0.139). All BMFO films with frequencies higher than 510 kHz show a significant increase in tan δ, which may be attributed to the switches of dipoles in the films that cannot follow the change of the applied electric field at high frequency [27].

In this study, detailed data values of dielectric constant, dielectric loss, residual remnant polarization, coercive electric field and leakage-current density of the BMFO films are listed in Table 1, respectively. From these research results, it is clearly found that the BMFO film can greatly optimize the dielectric, ferroelectric and electrical properties of the sample under the appropriate Mg (x = 0.06) doping amount.

| Bi_{1-x}Mg_xFeO_3 | 2 Pr (µC/cm²) | 2 Ec (kV/cm) | J (A/cm²) | ε_r | tan δ |
|-------------------|---------------|--------------|-----------|-----|------|
| X = 0             | 120           | 48           | 5.86 × 10^{-4} | 22.2 | 0.139 |
| X = 0.02          | 124           | 40           | 6.55 × 10^{-6} | 36.76 | 0.084 |
| X = 0.04          | 130           | 39.3         | 8.89 × 10^{-7} | 37.25 | 0.060 |
| X = 0.06          | 140           | 38           | 3.73 × 10^{-7} | 55.29 | 0.051 |
| X = 0.08          | 90            | 24           | 7.69 × 10^{-5} | 28.23 | 0.223 |

The leakage-current behaviors of BFMO (x = 0.06) film was investigated further on the relationship between the leakage-current density (J) and electric field (E), for example the ln J vs. E^{1/2} plots, as shown in Figure 4. From the curves, we found that the leakage-current density is linearly related to the square root of the applied electric field. The linear variations of the current were usually corresponded either to the Schottky emission [28,29] or Poole–Frenkel emission [28,30]. The current resulting from Schottky–Richardson emission was controlled by the electrons flowing across the potential energy barrier via field-assisted lowering at a metal–insulator interface. The current density (J) in the Schottky emission can be expressed by the following equation [29]:

\[ J = A^* T^2 \exp \left( \frac{\beta_s E^{1/2} - \phi_s}{k_B T} \right) \]  

(1)

where \( \beta_s = (e^3/4\pi\varepsilon_0)^{1/2} \), \( e \) is the electron charge, \( \varepsilon_0 \) is the dielectric constant of free space, \( A^* \) is the effective Richardson constant, \( T \) is the absolute temperature, \( E \) is the applied electric field, \( \phi_s \) is the contact potential barrier, and \( k_B \) is the Boltzmann constant. Poole–Frenkel emission was due to field-enhanced thermal excitation of trapped electrons from the valence band into the conduction band. The current density can be given by [30]

\[ J = J_0 \exp \left( \frac{\beta_{PF} E^{1/2} - \phi_{PF}}{k_B T} \right) \]  

(2)

where \( J_0 = \sigma_0 E \) is the low-field current density, \( \beta_{PF} = (e^3/\pi\varepsilon_0 E)^{1/2} \), \( \sigma_0 \) is the low-field conductivity, \( \phi_{PF} \) is the height of trap potential well.
which means that there is no effect on ferroelectric properties under bending. Just like flexible lead-free BaTiO$_3$ ferroelectric elements also have similar results [31].
which shows the insulating property nearly remains unchanged. These results show that the effect of physical bending on the leakage-current behavior of the film is negligible [32].

Figure 5. (a) Schematic diagrams showing the measurements structure and (b) ferroelectric hysteresis loops under different bending conditions of the flexible Ag/BMFO/FSS films.

For enhanced the practicability, BMFO (x = 0.06) film was prepared in the flexible equipment system. At different bending radius and applied electric fields, the leakage-current density was measured, as shown in Figure 6. From the measurement results, the BMFO (x = 0.06) film under different bending conditions flat, r = 12 mm, 10 mm and 6 mm can obtain the leakage-current density at 50 kV/cm of $3.73 \times 10^{-7}$, $3.91 \times 10^{-7}$, $4.08 \times 10^{-7}$, $4.27 \times 10^{-7}$ A/cm², respectively. From the inset in Figure 6, the leakage-current density of all samples is approximately $4.0 \times 10^{-7}$ A/cm² at 50 kV/cm, which shows the insulating property nearly remains unchanged. These results show that the effect of physical bending on the leakage-current behavior of the film is negligible [32].

Figure 6. Leakage-current density (J)–electric field (E) plots of the flexible BMFO (x = 0.06) film under different bending conditions. The inset shows the enlarged J–E plots around E = 50 kV/cm.

The long-term working reliability of materials is a very important factor for the practicality of microelectronic and storage memory devices. As shown in Figure 7, the residual polarization (2P_r) and leakage-current density (J) dependence on retention time were observed at the BMFO (x = 0.06) film with different bending conditions. From the measurement results, we clearly found that the sample under the different bending conditions of flat and r = 6 mm, the 2P_r and J values remained almost unchanged at retention time to $10^6$ s. It is worth noting from these results that the flat and bending BMFO film has excellent charge retention ability at room temperature, and the retention time can reach $10^6$ s. The curve between bending state and flat holding time almost overlaps, no
significant attenuation of polarization and leakage-current properties are found, indicating the ability to maintain bending stability of BMFO flexible film [33]. In order to optimize the practicality of the samples, we have developed novel BMFO films. A series of studies on the ferroelectric and electrical properties of these multiferric films under flat and different bending conditions were carried out and practical-grade results were obtained.

Figure 7. 2 Pr and leakage-current density retention measurements for the flexible BMFO (x = 0.06) film in flat and r = 6 mm.

4. Conclusions
High-quality BMFO films without bottom electrode processes were fabricated on FSS substrates. The effects of Mg-doping of BMFO films on ferroelectric, electrical and retention properties under unbent and different bending conditions were investigated in this research. The BMFO (x = 0.06) flat film had the best residual polarization value 140 μC/cm², a high dielectric constant 55.29 and the lowest leakage-current density of $3.73 \times 10^{-7}$ A/cm². Proper doping of Mg will decrease the lone pair activity of Bi$^{3+}$ ions and cause ferroelectric distortion, which will increase the residual polarization of the corresponding doped film. The leakage-current mechanisms of BMFO films obtained in the study were controlled by the Poole–Frenkel emission in the low-electric-field region, and the Schottky emission in the high-electric-field region. In addition, the excellent ferroelectric, leakage current, and retention characteristics of the BMFO films could be well maintained under different bending conditions. These findings prove that the flexible BMFO multi-ferroelectric films on FSS substrate have great potential for microelectronic device applications.

Author Contributions: H.-Z.C., D.-Y.L., M.-C.K. and P.-L.Z. conceived and designed the experiments. H.-Z.C. and M.-C.K. prepared the materials. P.-L.Z. performed the experiments. H.-Z.C., D.-Y.L. and P.-L.Z. analyzed data. H.-Z.C., D.-Y.L., M.-C.K. and P.-L.Z. wrote the manuscript. All authors have read and agreed to the published version of the manuscript.

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