Fabrication and characterization of compositionally graded $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin films

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An undoped BiFeO_3 thin film, Gd doped $\text{Bi}_{0.95}\text{Gd}_{0.05}\text{FeO}_3$ thin film with a constant composition, Gd up-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ and Gd down-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin films were successfully grown on Pt (111)/Ti/SiO₂/Si (100) substrates using a sol-gel and spin coating technique. The crystal structure, ferroelectric and dielectric characteristics as well as the leakage currents of these samples were thoroughly investigated. The XRD (X-Ray Diffraction) patterns indicate that all these thin films consist of solely perovskite phase with polycrystalline structure. No other secondary phases have been detected. Clear polarization-electric field (P-E) hysteresis loops of all these thin films demonstrate that the incorporation of Gd^{3+} into the Bi site of BFO thin film have enhanced the ferroelectric performance of pure BiFeO_3 thin film, and the Gd down-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin film has the best ferroelectric properties. Compared to other thin films, the optimal ferroelectric behavior of the Gd down-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin film results from its large dielectric constant, low dissipation factor and low leakage current.

Keywords: *Gd substituted BiFeO₃ thin films; crystal structure; ferroelectric properties; sol-gel technique*

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1. Introduction

In recent years, great attention has been paid to single-phase BiFeO_3 (BFO) multi-ferroic materials crystallized in the ABO_3 -type perovskite structure with the $R3c$ space group at room temperature, which display the co-existence of various competing orderings, such as ferromagnetic, ferroelectric, anti-ferromagnetic as well as elastic orders [1, 2]. The characteristics of BFO multi-ferroics promise potential applications in advanced magneto-electric devices and ferroelectric random access memories (FeRAMs) [3]. However, one of the drawbacks of these materials is their high leakage current at room temperature (RT). The high leakage current in BFO materials results in inferior ferroelectricity and reliability of FeRAMs [4]. It is well established that small amounts of Fe^{2+} and oxygen vacancies [V_O^{2-}] could be responsible for the high leakage currents in BFO materials [5]. As a result, a site engineering technique, consisting

in substitution of a small amount of Fe atoms by impurity atoms, has been used to reduce the leakage currents of BFO materials [6]. So far, several atoms including Mn [7] or Ti [8] have been substituted for Fe atoms (B sites), in order to restrain the valence fluctuation of Fe atoms, and thus to reduce the leakage current. At the same time, Bi atoms (A sites) substitution with non-volatile rare earth ions, such as La and Nd in BFO multi-ferroic materials, have been used to control the volatile nature of Bi and to suppress the generation of oxygen vacancies for charge compensation [9].

Recently, considering the fact that the ionic radius of Gd^{3+} (0.111 nm) is close to the ionic radius Bi^{3+} (0.120 nm) and the valence state of Gd ions is also identical to that of Bi ions, some studies regarding Gd atoms doping in BFO materials (Bi atom substitution with Gd) have been described in literature [10–12]. Gd doping could indeed decrease the leakage current in BFO materials, which is probably ascribed to the suppression of the impurity phases or the mobile defects such as Fe^{2+} ions or O and Bi vacancies [13]. In order to make use

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of the Gd doped BFO in the future multi-ferroics memory devices, it is necessary to search for an appropriate thin film growth technique for further decreasing the leakage current and improving the ferro-electricity of Gd doped BFO materials. In the present article, the structural, ferroelectric, dielectric properties, and leakage currents of compositional up-graded, down-graded $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ and Gd doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin films with a constant composition have been thoroughly investigated.

2. Experimental

Different kinds of samples, such as undoped BFO thin film, Gd doped $\text{Bi}_{0.95}\text{Gd}_{0.05}\text{FeO}_3$ thin film, Gd up-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin film with the Gd content increasing from the substrate surface to the thin film surface ($x = 0.025, 0.05, 0.075, 0.1$) and Gd down-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin film with the Gd content decreasing from the substrate surface to the thin film surface ($x = 0.025, 0.05, 0.075, 0.10$) were deposited onto Pt (111)/Ti/SiO₂/Si(100) substrates (200 nm Pt/40 nm Ti/500 nm SiO₂/Si (100)) using a sol-gel and spin coating technique, respectively. For simplicity, the above-mentioned different samples were referred to as: the pure BFO, $\text{Bi}_{0.95}\text{Gd}_{0.05}\text{FeO}_3$, Gd up-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$, and Gd down-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin films, respectively. The precursor solutions of the above-mentioned samples were prepared by dissolving $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ or $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in 2-methoxyethanol. Acetic anhydride was added as a dehydrating agent. The final concentration of precursor solutions was adjusted to 0.3 mol/L. The four different precursor solutions were successfully prepared under continuous stirring. After aging the films were deposited on the Pt (111)/Ti/SiO₂/Si (100) substrates via spin coating at 3300 rpm for 15 seconds. Each layer was hydrolyzed at 350 °C for 5 minutes and annealed at 500 °C for 5 minutes in the air. These steps were repeated 12 times to achieve an identical film thickness. The thickness of all these thin films was about 240 nm. Then, the final annealing at 600 °C for 30 minutes in the air was carried out. The final structures of the samples

are depicted in Fig. 1. The thickness of all thin films is about 200 nm. The crystal structures of the samples were investigated by the XRD method using a Cu $K\alpha_1$ ($\lambda = 0.15406$ nm) radiation at 40 kV and 30 mA with a multi-purpose XRD system (D/MAX-RB). For electrical measurements a gold thin film was coated on the surface of the samples with an area of $5.25 \times 10^{-5} \text{ cm}^{-2}$, using a shadow mask. After that the film was sintered at 550 °C for 15 minutes. The ferroelectric hysteresis loops and leakage currents of the films were obtained using a ferroelectric tester (Radiant Technologies, RT66A). The dielectric constants and the dissipation factors were measured using an HP4194A impedance analyzer. All the measurements were performed at room temperature.

(a) BiFeO₃ (BFO) thin film (twelve layers formed by spin coating)	(b) Bi_{0.95}Gd_{0.05}FeO₃ thin film (twelve layers formed by spin coating)
Pt(111)/Ti/SiO₂/Si(100)	Pt(111)/Ti/SiO₂/Si(100)
three layers BGFO (Gd content = 10 %)	three layers BGFO (Gd content = 2.5 %)
three layers BGFO (Gd content = 7.5 %)	three layers BGFO (Gd content = 5 %)
three layers BGFO (Gd content = 5 %)	three layers BGFO (Gd content = 7.5 %)
three layers BGFO (Gd content=2.5 %)	three layers BGFO (Gd content = 10 %)
(c) Pt(111)/Ti/SiO₂/Si(100)	(d) Pt(111)/Ti/SiO₂/Si(100)

Fig. 1. The scheme of sample structures grown on Pt (111)/Ti/SiO₂/Si (100) substrates: (a) pure BFO thin film; (b) $\text{Bi}_{0.95}\text{Gd}_{0.05}\text{FeO}_3$ thin film; (c) Gd up-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin film; (d) Gd down-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin film.

3. Results and discussion

Fig. 2 shows the XRD patterns of the pure BFO, $\text{Bi}_{0.95}\text{Gd}_{0.05}\text{FeO}_3$, Gd up-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$, and Gd down-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin films grown on Pt (111)/Ti/SiO₂/Si(100) substrates. All the diffraction peaks have been identified and indexed according to the standard diffraction pattern data (PCPDF200169) of a BFO powder. It can be seen

that all the films show the formation of solely perovskite phase with polycrystalline structure, and the peaks of well-documented impurity phases, such as $\text{Bi}_2\text{Fe}_4\text{O}_9$ (Fe-rich phase) and $\text{Bi}_{36}\text{Fe}_{24}\text{O}_{57}$ (Bi-rich phase), have not been detected [14]. In addition, only (110) and (211) diffraction peaks, obtained from the pure BFO, $\text{Bi}_{0.95}\text{Gd}_{0.05}\text{FeO}_3$, Gd up-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$, and Gd down-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin films, can be seen in Fig. 2. The (110)-orientation ratio can be calculated using equation 1 [15]:

$$\text{Orientation ratio} = \frac{I(110)_{\text{film}}}{I(110)_{\text{film}} + I(211)_{\text{film}}} \times 100 \% \quad (1)$$

where $I(110)$ and $I(211)$ refer to the peak intensity of the (110) and (211) orientations of the films. The (110)-orientation ratio of pure BFO, $\text{Bi}_{0.95}\text{Gd}_{0.05}\text{FeO}_3$, Gd up-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$, and Gd down-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin films is 78.7 %, 77.9 %, 72.78 % and 76.76 %, respectively. As a consequence, we conclude that the crystal structure of BFO film has not been affected by the incorporation of the Gd^{3+} ions and there is no isolated Gd in the matrix of the compound but it enters the lattice. In other words, the incorporation of Gd^{3+} into Bi site of BFO thin film, both with a fixed or graded doping, does not change the bismuth-layered perovskite structure.

The polarization-electric field (P-E) hysteresis loops of the pure BFO, $\text{Bi}_{0.95}\text{Gd}_{0.05}\text{FeO}_3$, Gd up-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$, and Gd down-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin films grown on Pt (111)/Ti/SiO₂/Si(100) substrates are shown in Fig. 3. Clear hysteresis loops are observed for all these thin film samples, which have a typical shape for ferroelectric materials. It is evident that for the pure BFO thin film, a ferroelectric hysteresis loop is observed with a remnant polarization ($2P_r$) of 10.18 $\mu\text{C}/\text{cm}^2$ and a coercive electric field ($2E_c$) of 280 kV/cm. When the substitution of a Bi site by Gd^{3+} ion with a concentration of 0.05 takes place, $2P_r$ value increases up to 19.96 $\mu\text{C}/\text{cm}^2$ and $2E_c$ value decreases to 217 kV/cm. Consequently, the incorporation of Gd^{3+} into the Bi site of a

Fig. 2. X-ray diffraction patterns of the pure BFO, $\text{Bi}_{0.95}\text{Gd}_{0.05}\text{FeO}_3$, Gd up-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ and Gd down-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin films, grown on Pt (111)/Ti/SiO₂/Si (100) substrates.

pure BFO thin film leads to the improvement of ferroelectric performance of the film. It is noted from Fig. 3 (c and d) that the ferroelectric behavior of Gd up-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ or Gd down-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin film, is superior to that of $\text{Bi}_{0.95}\text{Gd}_{0.05}\text{FeO}_3$ thin film. However, for Gd down-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin film, the ferroelectric hysteresis loop is optimal with a remnant polarization ($2P_r$) of 21.6 $\mu\text{C}/\text{cm}^2$ and a coercive electric field ($2E_c$) of 262 kV/cm. Compared to the saturation polarization value of pure BFO thin film, the enhanced saturation polarization values in $\text{Bi}_{0.95}\text{Gd}_{0.05}\text{FeO}_3$, Gd up-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$, and Gd down-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin films may probably be ascribed to their low leakage current densities, which is shown in Fig. 5.

Fig. 4 shows the variation of dielectric constant (ϵ_r) and dissipation factor ($\tan\delta$) as a function of applied frequency for the pure BFO, $\text{Bi}_{0.95}\text{Gd}_{0.05}\text{FeO}_3$, Gd up-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$, and Gd down-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin films, measured at room

Fig. 3. P-E hysteresis loops measured for: (a) the pure BFO; (b) $\text{Bi}_{0.95}\text{Gd}_{0.05}\text{FeO}_3$; (c) Gd up-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$, and (d) Gd down-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin films, grown on Pt (111)/Ti/SiO₂/Si (100) substrates.

temperature. With an increase of applied frequency in the range of 100 kHz to 1000 kHz, dielectric constants (ϵ_r) for all the thin films gradually decrease. This decrease in the dielectric constants is likely caused by space charge polarization or Maxwell Wagner type interfacial polarization [16]. At a fixed frequency, the dielectric constant (ϵ_r) of Gd down-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin films is the largest, which is beneficial to its optimal saturation polarization values ($2P_r$). On the other hand, at a fixed frequency, the dissipation factor ($\tan\delta$) of the Gd down-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin films, is also the lowest. Consequently, the largest value of dielectric constant of the Gd down-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin film coincides with the lowest dissipation factor. It is well-established that the ferroelectric material with a large dielectric constant and a low dissipation factor is advantageous for any device application.

Fig. 5 shows the I-V characteristics of Au/pure BFO/Pt, Au/ $\text{Bi}_{0.95}\text{Gd}_{0.05}\text{FeO}_3$ /Pt, Au/Gd up-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ /Pt and Au/Gd down-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ /Pt capacitors.

Fig. 4. Dielectric constant and dissipation factor versus frequency for: (a) the pure BFO; (b) $\text{Bi}_{0.95}\text{Gd}_{0.05}\text{FeO}_3$; (c) Gd up-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$, and (d) Gd down-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin films, grown on Pt (111)/Ti/SiO₂/Si (100) substrates.

The leakage current density of all the capacitors increases rapidly with an increase in the applied electric field. The leakage current densities of all the capacitors are less than $1.3 \times 10^{-5} \text{ A}/\text{cm}^2$ at the maximum applied field of 180 kV/cm. Compared to the leakage current density in the Au/pure BFO/Pt capacitor measured at a fixed applied electric field, the densities of leakage currents in the Au/ $\text{Bi}_{0.95}\text{Gd}_{0.05}\text{FeO}_3$ /Pt, Au/Gd up-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ /Pt or Au/Gd down-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ /Pt capacitors are significantly decreased. The lowest leakage current density has been measured in the Au/Gd down-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ /Pt capacitors. The values of leakage current densities in the four capacitors shown in Fig. 5 are also in good agreement with the dielectric loss values of the pure BFO, $\text{Bi}_{0.95}\text{Gd}_{0.05}\text{FeO}_3$, Gd up-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$, and Gd down-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin films shown in Fig. 4. The low leakage currents in BiFeO_3 thin films are probably connected with their low dielectric loss at a low frequency at room temperature, which has been described in [17]. Therefore, it is reasonable to infer that, compared to other samples, the lowest dielectric loss in the Gd down-graded doped $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ thin film corresponds to the lowest leakage current of the film.

Fig. 5. I-V characteristics of the Au/pure BFO/Pt, Au/Bi_{0.95}Gd_{0.05}FeO₃/Pt, Au/Gd up-graded doped Bi_{1-x}Gd_xFeO₃/Pt, and Au/Gd down-graded doped Bi_{1-x}Gd_xFeO₃/Pt capacitors.

4. Conclusions

In summary, the pure BFO, Bi_{0.95}Gd_{0.05}FeO₃, Gd up-graded doped Bi_{1-x}Gd_xFeO₃, and Gd down-graded doped Bi_{1-x}Gd_xFeO₃ thin films grown on Pt (111)/Ti/SiO₂/Si (100) substrates were synthesized by a sol-gel and a spin-coating method. Varying the substitution of Bi sites in BFO thin films by Gd³⁺ ions did not cause any significant change in the perovskite phase polycrystalline structure of all the films. Room temperature polarization measurements clearly showed an improvement in ferroelectric behavior of the BFO caused by Gd substitution. The optimal ferroelectric hysteresis loop with a remnant polarization (2P_r) of 21.6 μC/cm² and a coercive electric field (2E_c) of 262 kV/cm were obtained for Gd down-graded doped Bi_{1-x}Gd_xFeO₃ thin film, respectively. It is worth noting that, compared to other thin films, the Gd down-graded doped Bi_{1-x}Gd_xFeO₃ thin film had the largest value of dielectric constant and the lowest dissipation factor, which also resulted in the lowest leakage current density in the film. Our experimental results demonstrate that Gd down-graded doped Bi_{1-x}Gd_xFeO₃ thin films are very promising for the application in the future ferroelectric memory devices.

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