

Electrical and magnetic properties of $\text{BiFe}_{0.97-x}\text{Mn}_{0.03}\text{Zn}_x\text{O}_3$ thin films with different Zn content synthesized by chemical solution deposition (CSD)

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$\text{BiFe}_{0.97-x}\text{Mn}_{0.03}\text{Zn}_x\text{O}_3$ (BFMZ) thin films with various Zn contents ($x = 0, 0.01, 0.02, 0.05$, and 0.1) were prepared on Pt/Ti/SiO₂/Si (100) substrates by a chemical solution deposition (CSD) technique. The crystal structures of BFMZ thin films were analyzed by X-ray diffraction (XRD). The effects of the Zn content on the magnetic, dielectric properties, and leakage current of these BFMZ films were thoroughly investigated. The analysis by XRD demonstrated that all the BFMZ thin films were of a polycrystalline rhombohedral perovskite structure with the space group R3c. For the BFMZ thin films, slim magnetic hysteresis (M-H) loops were observed, and the saturated magnetization (M_s) of the BFMZ thin film increased with an increase of the Zn content. Compared to the other BFMZ thin films with Zn content between 0.01 and 0.1, the BFMZ thin film with Zn content $x = 0$ has the largest dielectric constant and the smallest dielectric loss. In addition, With co-doping of Mn^{2+} and Zn^{2+} ions at Fe^{3+} sites in the BFMZ thin films, the leakage current density increased with an increase of the Zn concentration in the films.

Key words: $\text{BiFe}_{0.97-x}\text{Mn}_{0.03-x}\text{Zn}_x\text{O}_3$ films, Ferroelectrics properties, Magnetic properties, Chemical solution deposition

Introduction

In recent years, significant attention has been paid to multiferroic materials which display the co-existence of various competing orderings, such as ferromagnetic, ferroelectric, antiferromagnetic, as well as elastic orders [1, 2]. The characteristic of multiferroics promise potential applications in advanced magnetoelectric devices and ferroelectric random access memories. One of the well-known multiferroics, BiFeO_3 (BFO), exhibits the co-existence of ferroelectric and G-type antiferromagnetic order above room temperature and a purported magnetoelectric coupling between spin and polarization [3]. Though as promising as BFO is, some drawbacks such as a high leakage current, small spontaneous polarization (P_s) and remnant polarization (P_r), and high coercive field of BFO thin films, are known to be serious problems, which could hinder their future applications in multiferroic devices [4]. It has been reported that small amounts of Fe^{2+} and oxygen vacancies [V_{O}^{2-}] may be responsible for the high leakage current in BFO [5]. Based on this assumption, a site engineering technique by substitution of a small amount of impurities is proposed to reduce the leakage current of BFO [6]. Bi-site substitution with La and Nd atoms to controll volatile Bi atoms and to suppress generation of oxygen vacancies have been attempted in BFO thin films. However, Bi-site substitution with La and Nd atoms also reduces P_r in the BFO thin films [7, 8]. On the other hand, Fe-site substitution with donor

atoms such as Nb and Mn atoms to fill oxygen vacancies has also been reported [9, 10]. At the same time, Mn-substituted $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ thin films grown on Pt/Ti/SiO₂/Si (100) substrates using chemical solution deposition were thoroughly studied by Singh *et al.* [11]. Their research findings demonstrates that Mn substitution could improve the breakdown characteristics of the BFO thin films and the leakage currents densities in the 3% and 5% Mn-substituted films were lower than that in pure BFO films at an applied electric field of 1 MV/cm at RT (room temperature). In addition, Fe-site substitution with Ti^{4+} or Zn^{2+} to reduce the leakage current in BFO thin films has also been reported in the literature [12]. However, as is pointed out by some groups [13, 14], it is not easy to reduce the leakage current of BFO films by a single ion-doping method since an excess substitution causes an increase in the leakage current in the films. Therefore, Mn and Ti co-doped BFO thin films with an improved leakage current was described by Kawae *et al.* [15]. In this work, we report on an alternative route, i.e., the synthesis and characterization of (Mn,Zn)-co-doped BFO (BFMZ) thin films with co-doping of Mn^{3+} and Zn^{2+} ions at Fe^{3+} sites.

Experimental Procedure

A sol-gel spin-coating technique was employed to fabricate BFMZ thin films ($x = 0, 0.01, 0.02, 0.05$, and 0.1) on Pt/Ti/SiO₂/Si (100) substrates. The sols were obtained from bismuth nitrate [$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$] (Aldrich, 99.99%), iron nitrate, zinc nitrate, and manganese acetate [$\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$] which were used as solutes, and 2-methoxyethanol as solvent. 10% excess of bismuth nitrate was added to compensate for possible bismuth loss during the high

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temperature process. The final concentration of precursor solutions was approximately 0.2 mol/l. Prior to preparing the BFMZ thin films, the Pt/Ti/SiO₂/Si (100) substrates were cleaned by ultra-sonication in acetone and alcohol and dried with nitrogen gas. And then, the precursor solutions were spin-coated on the cleaned Pt/Ti/SiO₂/Si (100) substrates at a rate of 5000 rpm for 30 s. The wet films were preheated over a hot-plate at 180 °C for 5 minutes and followed by a pyrolysis process at 350 °C for 5 minutes. The coating and thermal treatment process was repeated twelve times. Finally, the resultant films were annealed at 600 °C for 5 minutes in air by a rapid thermal annealing process for full crystallization. X-ray diffraction (XRD) (Rigaku Dmax/RB) with Cu K α radiation was used for phase analysis of BFMZ thin films. For electrical measurements, Pt was coated by DC sputtering on the surface of the BFMZ thin films with an area of $5.25 \times 10^{-5} \text{ cm}^2$ using a shadow mask. The ferroelectric hysteresis loops and leakage current behaviors of the films were obtained using a ferroelectric tester (Radiant Technologies, RT66A). The dielectric constant and the dissipation factor were measured using an HP4194A impedance analyzer. The high frequency capacitance-voltage characteristics of BFMZ thin films were measured using a Keithley 590 CV analyzer at 1 MHz with a bias sweep rate of 0.2 V/s. A vibrating sample magnetometer (VSM) was used to measure the magnetic properties. All the measurements were performed at room temperature.

Results and Discussion

Fig. 1 shows the XRD patterns of BFMZ thin films with various Zn contents ($x = 0, 0.01, 0.02, 0.05$, and 0.1). A polycrystalline rhombohedral perovskite structure with the space group R3c can be well indexed in the pattern of the pure BFO (JCPDS Card No. 72-2493). However, the peaks of impurity phases such as $\text{Bi}_2\text{Fe}_4\text{O}_9$ and Fe_2O_3 resulting from Bi deficiency were not detected. On the other hand, it is clear that the intensity of both the (200) and (100) diffraction peaks for BFMZ thin films increases with an increase of the Zn content in the BFMZ thin films. In the case of the XRD patterns of the Mn-substituted BFO thin films formed by depositing a sol-gel chemical solution on Pt/Ti/SiO₂/Si (100) structures, Singh *et al.* have pointed out that the structure of Mn-substituted BFO thin films are of the distorted rhombohedral R3c structure [11]. In this study, we can conclude that the co-substitution of Mn and Zn in BFO thin films could keep the R3c structure of BFO being unchanged.

The magnetic hysteresis (M-H) loops of BFMZ thin films with various Zn contents ($x = 0, 0.01, 0.02, 0.05$, and 0.1) measured by a VSM with an in-plane mode, is shown in Fig. 2. All the BFMZ thin films exhibit weak magnetization in slim magnetic loops with saturated magnetization (Ms) of about 25.79, 32.91, 38.79, 40.57 and 43.55 emu/cm³ with the change of Zn content from 0 to 0.1, respectively. Compared with pure BFMO thin

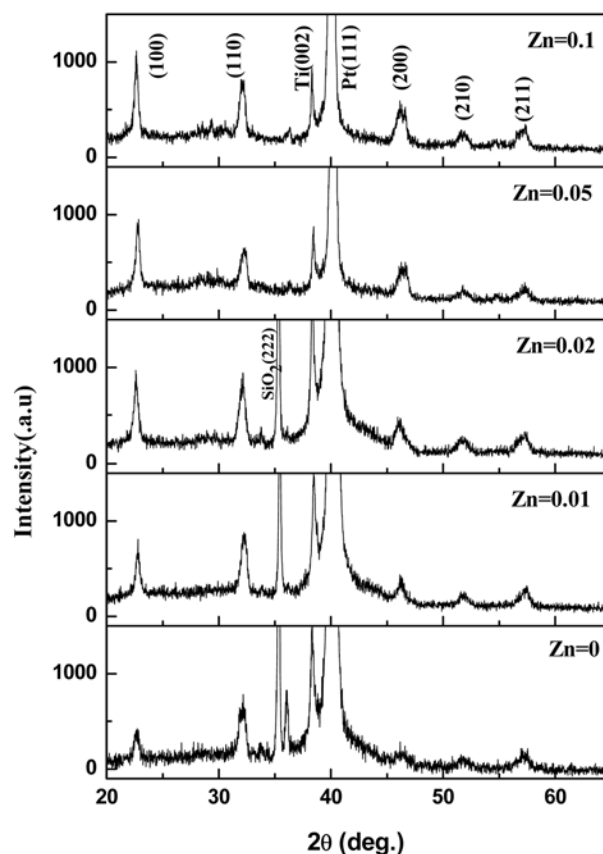


Fig. 1. X-ray diffraction patterns of $\text{BiFe}_{0.97-x}\text{Mn}_{0.03}\text{Zn}_x\text{O}_3$ thin films on Pt/Ti/SiO₂/Si substrates for compositions $x = 0, 0.01, 0.02, 0.05$, and 0.1 .

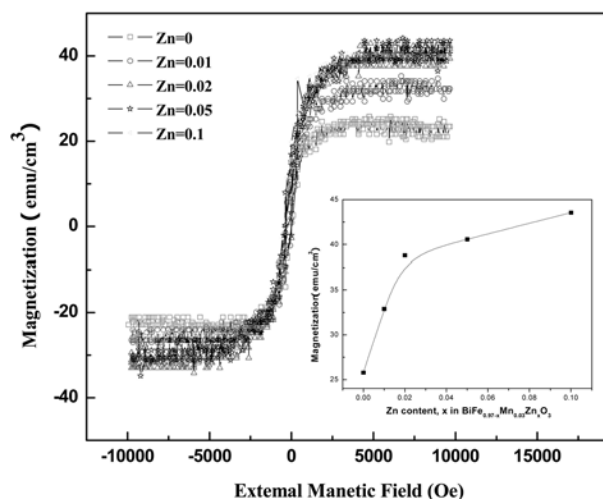


Fig. 2. Magnetic properties of $\text{BiFe}_{0.97-x}\text{Mn}_{0.03}\text{Zn}_x\text{O}_3$ thin films on Pt/Ti/SiO₂/Si substrates for compositions $x = 0, 0.01, 0.02, 0.05$, and 0.1 .

film with a Mn content of about 0.03, substituting Fe ions with nonmagnetic Zn^{2+} ions would increase the magnetization of the BFMO thin films. As is shown in the inset of Fig. 2, the saturated magnetization (Ms) of the BFMZ thin films increases with an increase of the Zn content between 0 and 0.1.

Fig. 3 shows the variation of dielectric constant (ϵ_r) and dissipation factor ($\tan\delta$) as a function of applied frequency for the BFMZ films with various Zn contents ($x = 0, 0.01, 0.02, 0.05$, and 0.1) measured at room temperature. There is a decreasing tendency for the dielectric constant (ϵ_r) of the BFMZ thin films with a variation of the applied frequency from 10^3 Hz to 10^6 Hz. In addition, as is shown in Fig. 3, the dielectric constant (ϵ_r) of the BFMZ thin films obviously decreases with an increase of the Zn content in the BFMZ thin films under an identical applied frequency. On the other hand, the dissipation factors ($\tan\delta$) for all the the BFMZ films with various Zn contents ($x = 0, 0.01, 0.02, 0.05$, and 0.1) shows a marked increase when the applied frequency is varied from 10^5 Hz to 10^6 Hz. As is shown in Fig. 3, the dissipation factors ($\tan\delta$) of the BFMZ thin films increase with an increase of the Zn content in the BFMZ thin films under an identical applied frequency.

Fig. 4 shows the leakage currents for the $\text{BiFe}_{0.97-x}\text{Mn}_{0.03}\text{Zn}_x\text{O}_3$

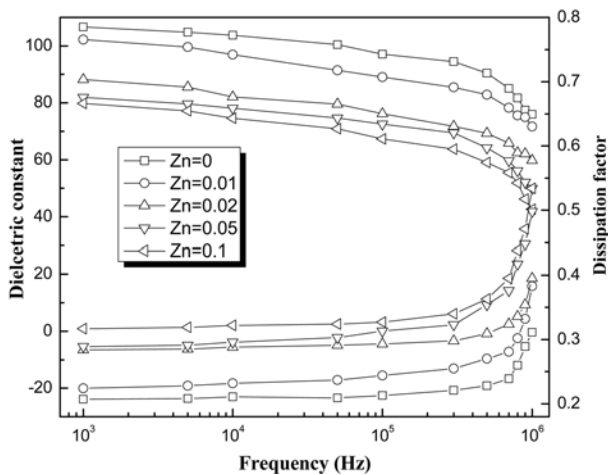


Fig. 3. Dielectric properties of $\text{BiFe}_{0.97-x}\text{Mn}_{0.03}\text{Zn}_x\text{O}_3$ thin films on Pt/Ti/SiO₂/Si substrates for compositions $x = 0, 0.01, 0.02, 0.05$, and 0.1 .

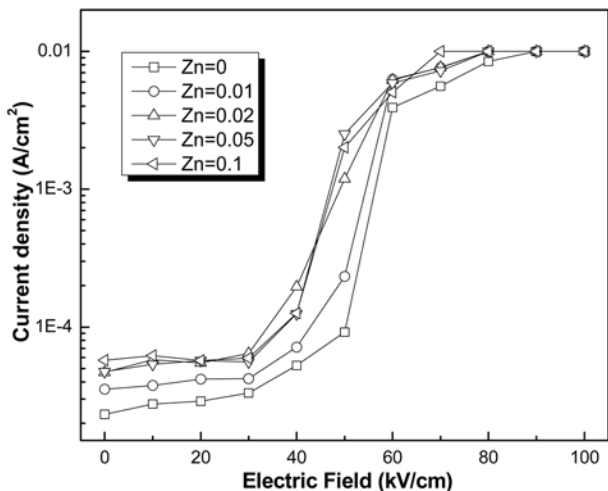


Fig. 4. Current leakage properties of $\text{BiFe}_{0.97-x}\text{Mn}_{0.03}\text{Zn}_x\text{O}_3$ thin films on Pt/Ti/SiO₂/Si substrates for compositions $x = 0, 0.01, 0.02, 0.05$, and 0.1 as a function of the electric field.

$\text{Mn}_{0.03}\text{Zn}_x\text{O}_3$ films with the composition of $x = 0, 0.01, 0.02, 0.05$, and 0.1 as a function of the electric field. The leakage current density of all the films increases gradually with the applied electric field. It is worth noting that under an identical applied electric field, the leakage current density of the BFMZ thin films increases with an increase of the Zn content. For example, the 9.19×10^{-5} A/cm² leakage current density of the BFMZ thin film with Zn content $x = 0$ is less than that of BFMZ thin films with other Zn contents ($x = 0.01, 0.02, 0.05$, and 0.1) at an applied field around 50 kV/cm. That is to say, contrary to the results reported by Qi *et al.* [16], the leakage current in BFMZ thin films with Zn contents ($x = 0.01, 0.02, 0.05$, and 0.1) is higher than that in BFMZ thin film with Zn content ($x = 0$). The characteristic of the leakage current in the BFMZ thin films under an applied electric field shown in Fig. 4 should be probably ascribed to the variation of defect complexes between the acceptors [$(A_{\text{Fe}^{3+}}^{2+})'$] and $(V_{\text{O}^{2-}})^{\bullet\bullet}$ formed in Mn and Zn-ion-doped BFO thin films, which has also been reported in the literature [14]. In BFMZ thin films with Zn contents ($x = 0.01, 0.02, 0.05$, and 0.1), there exist defect complexes between $(\text{Zn}_{\text{Fe}^{3+}}^{2+})'$ and $(V_{\text{O}^{2-}})^{\bullet\bullet}$. When the site of Fe^{3+} substitution by Mn^{2+} is fixed, with an increase of Zn^{2+} ions in BFMZ thin films, the $(V_{\text{O}^{2-}})^{\bullet\bullet}$ will gradually release from the complexes of [$(\text{Zn}_{\text{Fe}^{3+}}^{2+})' - (V_{\text{O}^{2-}})^{\bullet\bullet}$], which bring about the increase of the leakage current in BFMZ thin films.

Conclusions

In conclusion, BFMZ thin films with various Zn contents ($x = 0, 0.01, 0.02, 0.05$, and 0.1) have been formed on Pt (111)/Ti/SiO₂/Si (100) substrates by CSD using a repeated coating/drying cycle. The effects of the Zn content of BFMZ thin films on XRD, magnetic hysteresis (M-H) loops, I-V, dielectric constant and loss characteristics were thoroughly investigated. The XRD results indicate that all the BFMZ thin films had a well-defined rhombohedral perovskite structure and no secondary phases. In BFMZ thin films, slim magnetic hysteresis (M-H) loops are observed, and the saturated magnetization (M_s) of the BFMZ thin film increases with an increase of the Zn content. The dielectric constant and loss measurement indicate that the BFMZ thin film with $x = 0$ of Zn content has the largest dielectric constant and the smallest dielectric loss. In addition, by co-doping of Mn^{2+} and Zn^{2+} ions at Fe^{3+} sites in the BFMZ thin films, the leakage current density increased with an increase of the Zn concentration in the films. Our results suggest that a larger ϵ_r , a small $\tan\delta$, a low leakage current, a better M-H loops can not readily be realized in Mn and Zn co-doped BiFeO_3 thin films.

Acknowledgments

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