Significantly reduced leakage current density in Mn-doped BiFeO$_3$ thin films deposited using spin coating technique

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Abstract: BiFeO$_3$ (BFO) and Mn-doped BFO thin films are prepared on indium tin oxide/glass substrates using wet chemical deposition technique. The role of Mn defects (3% to 10%) on the leakage current density and other physical properties of BFO thin film devices is investigated. The X-ray diffraction patterns confirm the single-phase formation of rhombohedrally distorted BFO thin films. The scanning electron microscopy images approve uniform and crack-free film depositions, which is of great importance to the practical device applications of such materials. The oxidation states are determined by X-ray photoelectron spectroscopy (XPS). These XPS results reveal the presence of multiple valence states of Fe ions (Fe$^{2+}$, Fe$^{3+}$) and Mn (Mn$^{3+}$, Mn$^{4+}$) ions, which play a decisive role in determining the leakage current density. However, the Mn-doping at the Fe site in BFO reduces oxygen vacancies and Fe$^{2+}$ states, hence suppressing the leakage current density. The leakage current density is reduced by three orders of magnitude ($10^{-4} – 10^{-7}$ A/cm$^2$), upon Mn-doping as clearly demonstrated by J-V characteristics. These results indicate that the primary contributors to the conduction in BFO based thin films are oxygen vacancies and the Fe$^{2+}$ states in these devices.

1. Introduction

Multiferroic BiFeO$_3$ (BFO) has attracted keen attention because of its intriguing material features, such as co-existence of ferroelectricity and anti-ferromagnetic ordering, substantial remnant polarization, high Curie temperature ($T_c = 830$ °C), and high Neel temperature ($T_N = 370$ °C) [1]. In fact, the relatively lower bandgap (2.1 – 2.7) eV, and high spontaneous polarization (ranging from 50 – 100 µC/cm$^2$ ) of BFO, approves its applicability in various research areas, particularly towards optoelectronics, photovoltaics, and memory applications [2,3]. Although BFO thin films exhibit excellent ferroelectric and optical features, several problems make them unsuitable for practical device applications. The two major limitations are; (i) single phase formation of BFO and (ii) larger leakage current density [4–6]. The former problem arises due to several reasons, such as the kinetics of formations and the volatile nature of bismuth. At the same time, the latter one is induced mainly due to the multiple valence states of Fe ion, presence of oxygen vacancies, and secondary phases, if any. To overcome the former limitation, several research groups have fabricated pure phase BFO using some advanced techniques (such as PLD, RF-sputtering, and CVD) [1,7,8]. However, to overcome the second major limitation of leakage current, doping at the Bi and Fe site with transition metal ions is
Qi et al. reported a significant reduction in resistivity by more than three orders upon 2 mol % Ti$^{4+}$ doping at the Fe site of BFO. They also report a massive enhancement in the resistivity values (almost two orders of magnitude) upon doping with Ni$^{2+}$ ions [6]. These results clearly indicate that the dopants play a decisive role in determining the conduction properties of BFO films.

Here, we report a simple and cost-effective fabrication process for depositing BFO thin films on ITO/glass substrates. The prime focus of the current work is to understand the relationship between the Mn-doping and electrical conductivity in single-phase BFO thin films. Doping at the Fe site with Mn-ion appears advantageous in several ways, such as reducing leakage current density by suppressing Fe$^{2+}$ states and reducing the oxygen vacancies. Additionally, Mn-doping may also improve the magnetic and electric behaviour in BFO films, which is not the domain of the current work [9]. Here we doped the Fe site in BFO films with the different concentrations of Mn ions (3 mol%, 5 mol%, 10 mol%) and measured the J-V characteristics of each device. These investigations provide a critical understanding of the cause of high leakage current BFO thin films.

2. Experimental Procedure

2.1. Materials and Methods:

Pure and Mn-doped BFO thin films are fabricated on ITO/glass substrates using chemical solution followed by the spin-coating deposition technique. To begin with, bismuth nitrate pentahydrate, iron nitrate nonahydrate, and manganese acetate dehydrate precursors are dissolved in a mixed solvent of water and 2-methoxyethanol. The precursor solution is prepared by vigorous stirring for an hour. Meanwhile, citric acid and nitric acid are also added to the solution while stirring at a temperature of 100 $^\circ$C. The obtained solution was kept for ageing for about 12 hours, and finally, the film deposition was carried out layer by layer, using the spin coating technique. In order to carry out a smooth and uniform deposition process, all the spinning parameters (spinning rate, spinning time, acceleration time) and the number of coatings were optimized. The deposited films were dried for 20 minutes (for 10 minutes each at two different stages of the deposition process) at 300 $^\circ$C. Finally, the prepared films were annealed at 600 $^\circ$C for 30 minutes in the air, using a tubular furnace.

2.2. Characterizations:

An image of the actual device and the schematic of the fabricated device are shown in Figs. 1a and 1b respectively. The top Al electrodes (circular) were deposited by employing the e-beam technique and circular shadow masks. The phase identification and crystalline structure were determined using an X-ray diffractometer (Rigaku Ultima-IV, Cu-ka radiation source, $\lambda = 1.5406$ Å). The surface smoothness, surface morphology, and cross-sectional view were examined using a field emission scanning electron microscope (Apreo LoVac) (FESEM). The chemical composition of all the constituents and the dopant distributions studies were estimated from the energy-dispersive X-ray spectroscopy (EDS unit attached to the FESEM Apreo LoVac instrument). X-ray photoelectron spectroscopy studies were carried out to determine the valence states of all the constituents. (Thermo Scientific K-Alpha). Finally, the dark J-V characteristic measurements were carried out using a Keysight source meter (Keysight B2912A).
3. Results and Discussions

3.1. XRD Analysis

Figure 2 shows the XRD patterns of the pure and Mn-doped BFO thin films deposited on ITO/glass substrates. These diffraction patterns matched well with the distorted perovskite structure of BFO. No additional phase appeared in any of the prepared films, which lends support to the simple, cost-effective, and pure phase fabrication process [10]. Moreover, due to the difference in the ionic radii and the valence state charge of the host (Fe) and the dopant (Mn) ions, a detectable distortion was observed from the XRD patterns (which results in a partial and complete structural transition from rhombohedral to orthorhombic). The structural distortion was also estimated using the Goldschmidt tolerance factor [11]. The Goldschmidt tolerance factor \( t \) helps in predicting the structural stability of perovskites which is given as

\[
t = \frac{r_A + r_O}{\sqrt{2} [r_B + r_O]}
\]

Where, \( r_A \), \( r_B \), and \( r_O \) are effective ionic radii of site A (Bi\(^{3+}\)), site B (Fe\(^{3+}\)), and oxygen ion respectively. After substituting the effective radii values of A and B, the above expression, in this case, becomes

\[
t = \frac{r_{Bi} + r_O}{\sqrt{2} [(1-x) r_{Fe} + x r_{Mn} + r_O]}
\]

Here, by taking \( r_{Bi} \), \( r_{Fe} \), \( r_{Mn} \) and \( r_O \) as 1.17 Å, 0.645 Å, 0.58 Å, and 1.38 Å, respectively, and the value of \( x \) from 0 to 0.1, we calculated the \( t \) values of all the prepared films and the evaluated values are given in Table 1. Usually, the value of \( t \) determines the stability of the perovskites. When the value of the \( t \) is close to 1, stabler perovskite phase will be formed and vice versa. Interestingly, we observed that the tolerance factor increased from 0.890 (BFO) to 0.893 (Bi Fe\(_{0.9}\) Mn\(_{0.1}\)O\(_3\)) with increasing the doping concentration, which indicates that Mn-doping improves the structural stability of the BFO crystals.
Figure 2. XRD patterns of BiFe$_{1-x}$Mn$_x$O$_3$ (a) $x = 0.00$, (b) $x = 0.03$, (c) $x = 0.05$, and (d) $x = 0.10$. Moreover, the average crystallite size was estimated using Scherrer’s equation and was found to be in the range of 19 nm to 24 nm [12]. The estimated crystallite sizes showed a non-monotonic variation with doping concentration. The crystallite sizes and the tolerance factor values of all the specimens are given in Table 1.

Table 1. shows the crystallite sizes and tolerance factor values of undoped and Mn-doped BFO thin films

| Composition | Crystallite size (nm) | Tolerance factor |
|-------------|-----------------------|-----------------|
| $x = 0.00$  | 23                    | 0.890           |
| $x = 0.03$  | 25                    | 0.891           |
| $x = 0.05$  | 20                    | 0.892           |
| $x = 0.10$  | 17                    | 0.893           |

3.2. Morphological studies

Figures 3 (a - d) show the plane FESEM images of the pure and Mn-doped BFO thin films. These images clearly indicate the crack-free and smooth deposition of all the compositions. Moreover, with the increase in Mn-concentration, the granular size increased, and the grains appeared more densely packed in the doped films compared to the pure films. However, we noticed some gaps in the pure BFO and 3 mol % Mn-doped BFO films. Moreover, figure 3(e) depicts the cross-section images of the pure BFO thin film. The average film thickness estimated from the cross-sectional images was found to be 320 ± 20 nm.
Figure 3. FESEM micrographs of BiFe\textsubscript{(1-x)}Mn\textsubscript{x}O\textsubscript{3} (a) x = 0.00, (b) x = 0.03, (c) x = 0.05, (d) x = 0.10, and (e) cross sectional view of BFO film

To further analyze the distribution of the Mn-dopant, we recorded the elemental mapping images as shown in figure 4. These images confirm the presence of all the constituents, including the Mn-dopants, and validate the absence of any other foreign constituent in the prepared films. In addition to this, the uniform spread of the yellow colour indicates the uniform distribution of the dopant throughout the sample, which is important for efficient device performance.

Figure 4. Elemental mapping images of constituent elements in 10 mol\% Mn-doped BFO film (a) Bi, (b) Fe, (c) Mn, (d) O, and (e) all constituents mixed

3.3. J - V characteristics

Figure 5 shows the current density versus voltage (J - V) curves of all the prepared thin film devices (Al/Mn-BFO/ITO/BFO) at room temperature. As predicted, rectifying behaviour was observed by applying the external bias voltage at ±1 V. The rectifying behaviour can be associated with the Schottky junction formation at Al/BFO and BFO/ITO interfaces. Moreover, with Mn-doping in BFO thin films, the leakage current density appears to reduce significantly. In particular, we found that the
leakage current density has reduced from $10^{-4}$ A/cm$^2$ to $10^{-7}$ A/cm$^2$ with Mn-doping, which is three orders of magnitude lower than the pure BFO films. Furthermore, the Mn-doping concentration and the leakage current density showed an inverse monotonic relation. These results clearly reveal that Mn-substitution is effective in suppressing the leakage current density in BFO films. Additionally, it was observed that the leakage current density increased with increasing bias voltage for all the fabricated devices. The improved resistive behaviour of the Mn-doped BFO films can be associated with several reasons, including a decrease in the concentration of oxygen vacancies, suppressing Fe$^{2+}$ formation, and improved microstructural properties [4,13].

The primary cause of leakage current in BFO thin films is mainly attributed to the presence of oxygen vacancies and Fe$^{2+}$ ions in the specimen. The Mn-doping in BFO tends to suppress the formation of these defective states. Usually, more oxidation state ion doping (say Ti$^{4+}$) compensates the charge by either of the following mechanisms; (i) by decreasing the cation valence (Fe$^{3+}$→Fe$^{2+}$) or ultimately creating cation vacancies, and (ii) filling the oxygen defects. Likewise, the doping of lower valence ions (such as Co$^{2+}$) compensates for the charge by either creating the oxygen defects or by increasing the cation valence (say Fe$^{3+}$→Fe$^{3+}$). However, it is complicated to estimate any particular mechanism for explaining the significant reduction in leakage current density of BFO with Mn-doping, owing to its multiple valence states of the host (Fe) and dopant ions (Mn). Therefore, we attempted to describe the possible mechanisms that reduced the conduction in these films.

Mn-doping suppresses the formation of oxygen vacancies, which are generated during the annealing process. These oxygen vacancies generate deep defect states within the sub-gap region, rendering the electrons to be mobile. Higher the oxygen vacancies, higher will be the free carriers generated in the device, which results in higher leakage current density. Moreover, these oxygen vacancies reduce the Fe$^{3+}$ into Fe$^{2+}$ in their vicinity, which develops major structural distortion and hence may induce poor insulating properties.

$$2\text{Fe}^{3+} + V_O^3 \rightarrow 2\text{Fe}^{2+}$$

![Figure 5](image-url)
The Mn-substitution reduces the concentration of oxygen vacancies, which can be understood by Kroger-Vink notation as given in equations 4 and 5. Likewise, if there exist the intrinsic Fe$^{2+}$ states (because of multiple valence states of Fe ion) in the specimen, Mn$^{3+}$-doping at the Fe$^{2+}$ site reduces the content of 2+ valence state ions. These defective Fe$^{2+}$ states generate more oxygen vacancies for charge compensation. Moreover, the presence of oxygen vacancies and defective Fe$^{2+}$ states may give rise to some secondary phases, which provide a conductive path for the carriers. Therefore, it is reasonable to reduce the leakage current density in BFO films with Mn-substitution

$$2\text{Fe}^{2+} + 2\text{Bi}^{3+} + 3\text{O}_{2}^{2-} \rightarrow 2\text{BiFeO}_{3} + V_{0} \left( \uparrow \frac{1}{2} \text{O}_{2} \right)$$  \hspace{1cm} (4)

$$\left(2\text{Mn}^{3+} \rightarrow 2\text{Fe}^{2+}\right) + 2\text{Bi}^{3+} + 3\text{O}_{2}^{2-} \rightarrow 2\text{Bi(Mn}_{\text{Fe}}\text{)}\text{O}_{3}$$  \hspace{1cm} (5)

Figure 6. Gaussian fitted XPS spectra of (a) Bi, (b) Fe, (c) Mn, and (d) O

To verify the valence states of all the constituents in BFO and Mn-doped BFO, we recorded XPS spectra of the pure and 10 mol % Mn-doped BFO thin films. Figure 6 (a - d) shows the XPS spectra of Bi 4f, Fe 2p, Mn 2p, and O 1s, respectively. Gaussian curve fitting was performed to deconvolute the XPS spectra to gain information about multiple oxidation states of the constituent elements of Mn-doped BFO. In figure 6 (a), the two peaks located at 158.73 eV and 163.9 eV correspond to Bi 4f$^{7/2}$ and Bi 4f$^{5/2}$, respectively [14]. Figure 6 (b) depicts the Fe 2p spectrum, in which the peaks were observed at 710.45 eV and 724.03 eV. These peaks correspond to Fe 2p$^{3/2}$ and Fe 2p$^{1/2}$, respectively [15]. Additionally, the Fe spectrum also shows two satellite peaks that can be ascribed to the presence of high spin Fe-O bonds. Upon deconvolution, the prominent peak splits to constituent peaks of Fe$^{2+}$ and Fe$^{3+}$, confirming the presence of multiple valence states of Fe ions in the prepared films. However, the concentration of the Fe$^{2+}$ states was found to decrease with Mn-doping. Figure 6 (c) illustrates the XPS spectrum of Mn 2p in which the peaks are located at 642.11 eV and 653.65 eV corresponding to 2p$^{3/2}$ state and 2p$^{1/2}$ state of Mn-ions [16]. By Gaussian curve fitting, these peaks split into their component peaks (Mn$^{3+}$ and Mn$^{4+}$), which approves the presence of trivalent and tetravalent oxidation states of Mn. Moreover, in figure 6 (d), the spectrum for O 1s is depicted, which shows two peaks at 529.5 eV and 530.9 eV, which indicate the presence of O 1s state and oxygen vacancies, respectively [17]. The XPS data analysis lends support to the above discussions based on conduction mechanisms. Therefore, Mn-
substitution in BFO is one of the most successful approaches in reducing the leakage current density in BFO thin films.

4. Conclusions

In summary, single-phase BFO and Mn-doped BFO thin films have been deposited on ITO/BFO substrate using a simple and cost-effective fabrication process. Mn-doping at the Fe site of BFO was found to be beneficial in improving the structural stability and morphological features. The leakage current density was reduced by three orders of magnitude with Mn-doping and showed an inverse correlation with the doping concentration. It is evident that the presence of divalent (Fe$^{2+}$) ions and oxygen vacancies are the main contributors to the leakage current density in BFO thin films; however, the individual effects of these defects in the conduction mechanism are yet to confirm. Indeed, the Mn-substitution makes this material suitable for practical device applications, particularly for photovoltaics.

Acknowledgement

The authors thank DST-SERB (EMR/2017-002340) for funding the project. The authors also acknowledge the BITS-Pilani Hyderabad campus for providing the cleanroom fabrication facilities and central analytical laboratory facilities to accomplish the work in due time. The authors would also like to thank Mrs. Renuka Hyder Khan, from EEE department, BITS – Pilani Hyderabad Campus for assisting in measuring the J-V characteristics of the fabricated devices.

Credit authorship contribution statement

Waseem Ahmad Wani- Conceptualization, Methodology, Investigation, Writing original draft, Formal analysis; Nilofar Naaz- Investigation, Writing original draft, Formal analysis; Souvik Kundu- Writing, review & editing; B. Harihara Venkataraman- Writing, review & editing; Kannan Ramaswamy- Writing, review, editing & supervision.

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