Multiferroic Consequence of Porous $(\text{BiFeO}_3)_x-(\text{BiCrO}_3)_{1-x}$ Composite Thin Films by Novel Sol–Gel Method

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Abstract In this work, we have presented a spin-coating method to produce thin films started with pure BiCrO_3 (BCO) and ended up with BiFeO_3 (BFO) by increasing x values in the $(\text{BiFeO}_3)_x-(\text{BiCrO}_3)_{1-x}$ composites. All the produced thin films have been crystallized at the annealing temperatures of 400 °C for 0.5 h. The XRD and EDAX spectrums give insight that the two crystal phases related to BCO and BFO stayed together within the thin film matrices. SEM analysis showed that the prepared composite had macroporous morphology with interconnected pores and its width (size) decreased with increasing x values. The strong correlations are observed among the microstructure, dielectric, ferroelectric, ferromagnetic properties and Fe concentration. Among all composites, the composition of 0.75 shows an attractive magnetization, polarization, switching and improved dielectric behaviors at room temperature. Significant increase in the multiferroic characteristics of 0.75 composition is due to arise of lower leakage current by causing reduction in oxygen vacancy density, and enhancement of super-exchange magnetic interaction between Fe^{3+} and Cr^{3+} at BFO/BCO interface layers. Our result shows that the thin layer on Pt (111)/Ti/SiO₂/Si substrate possesses simultaneously improved ferroelectric and ferromagnetic properties which make an inaccessible potential application for nonvolatile ferroelectric memories.

KEY WORDS: Multiferroic; Dual-phase composites; Spin-coating method; NV-Fe-RAM; PUND

1 Introduction

Recently, embedded memory in microcontrollers has become necessary to achieve high-speed access time and low-voltage operation for mobile computing.

Semiconductor memories such as dynamic random-access memory (DRAM) and static random-access memory (SRAM) are commonly utilized; however, these are volatile memory types whose data are lost when the power is shut down [1]. In contrast to these, the ferroelectric random access memory (Fe-RAM) is one of the alternative non-volatile memories that can replace the flash memory due to its fast speed, nonvolatility, high endurance and low operating voltage [2]. This technology is still available, but works effectively with occupying most of the useful space, and eventually gets discharged. Multiferroic materials with excellent magnetic and electric polarization at higher dielectric constant have recently attracted unprecedented attention. Since single-phase materials exist rarely in nature with such cross-coupling properties, an intensive research activity is being pursued toward the discovery of new multiferroic composite materials and the design of new engineered materials with strong magneto-electric (ME) coupling [3]. Generally, Bi-containing perovskites

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are promising candidates for multiferroic materials because of the presence of the stereochemically active lone electron pair of a Bi^{3+} ion [4]. Especially, BiFeO_3 (BFO) is a well-known multiferroic material, in which ferroelectric and antiferromagnetic domain coupling can be expected at room temperature (RT), owing to its high Curie temperature (T_c) of 1100 K, and its high Neel temperature (T_N) of 640 K [5]. In particular, the undesired high leakage current (due to its magnetic phases) remains an obstacle for improving the overall performance of device. To avoid the leakage problem, BiFeO_3 – BiCrO_3 nanocomposite films have been preferred as class of multiferroic materials for NV-Fe-RAM application. Singh *et al.* [6] reported that the leakage current density in BFO–BCO films decreased more than four orders of magnitude compared with those in BFO thin films at an applied electric field 600 kV/cm. Moreover, Cr ion-induced structural distortion in BFO would be expected to give lower leakage current and mainly originates from the ferromagnetic coupling among Fe^{3+} (d^5) and Cr^{3+} (d^3) under 180° [7]. BiCrO_3 (BCO) is a ABO_3 -type perovskite multiferroic material with active lone pair electrons on the A-site and a magnetic transition metal (Cr) on the B-site, similar to BFO [8]. Thin films of BCO have been reported to exhibit ferroelectric properties at room temperature and antiferroelectric properties at 10 K, indicating the existence of a phase transition [9]. Many research works were reported for the characterization of $\text{BiCrO}_3/\text{BiFeO}_3$ double-layered thin film over Pt/Ti/SiO₂/Si substrate by chemical solution deposition. These processes required larger time (3–3.5 h) for gel preparation, with high annealing temperature under the oxygen atmosphere [10]. We present a new approach for the deposition of nanostructured $\text{BiCrO}_3/\text{BiFeO}_3$ composite thin films on (111) Pt/Ti/SiO₂/Si substrate by spin-coating method at lower annealing temperature, time under an open atmosphere. Today, a wide variety of techniques are used for the preparation of $\text{BiCrO}_3/\text{BiFeO}_3$ thin films, including sputtering [11], molecular beam epitaxy [12], chemical vapor deposition [13] and spray pyrolysis [14]. Compared with other techniques, sol–gel spin-coating process is considered to be a trouble-free, less expensive and has an advantage of large area deposition with high facility of doping in fabricating thin films. In addition, some other research articles were also available for the $(\text{BiFeO}_3)_x$ – $(\text{BiCrO}_3)_{1-x}$ thin films grown on (100), (001) and (101) orientated platinum (Pt) substrates [15, 16]. The disadvantage of (100), (001) and (101) oriented substrate is that BiFeO_3 films grown on (111) have a rhombohedral structure, identical to that of single crystals, whereas films grown on (101) or (001) are monoclinically distorted from the rhombohedral by epitaxial constraint. The easy axis of spontaneous polarization lies close for (111), while

comparing with other oriented films. Most notable attention is paid in the (111) substrate due to its advantages of long-range cation ordering, with the reduction of cationic repulsion, shorter chemical bonds with smaller unit cell volumes [17]. In addition, (111) orientation has found to offer attractive dielectric properties compared to other crystalline orientation [18]. Previously, $\text{BiFe}_{1-x}\text{Cr}_x\text{O}_3$ thin films were grown only for low molar concentration ($x = 0, 0.03, 0.1, 0.2, 0.05, 0.5$) [19, 20] and obtained an antiferromagnetic property with less dielectric property. None had reported the higher-order molar concentration made on BFCO materials. In this study, $(\text{BiFeO}_3)_x$ – $(\text{BiCrO}_3)_{1-x}$ composite thin films were deposited on (111) oriented platinized silicon substrate by spin-coating method. The effect of molar concentration (with increasing x values) on the structural, morphological, electrical and multiferroic properties are discussed in detail. This work covers $(\text{BiFeO}_3)_x$ – $(\text{BiCrO}_3)_{1-x}$ composite which is a basic component in applications of ferroelectric random access memories (Fe-RAMs).

2 Experimental

The BFCO double-layered thin film obtained using a chemical solution deposition method was made on Pt (111)/Ti/SiO₂/Si substrate. Bismuth nitrate pentahydrate [$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$], iron nitrate nonahydrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] and chromium nitrate nonahydrate [$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] were used as raw materials. 2-methoxyethanol ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$) (2-MOE) was used as solvent and acetic acid was used as catalyst. 5% of excess Bi was added to compensate the bismuth loss during thermal annealing treatment, and the stirring was continued to form a homogeneous solution by keeping in a hot plate at 120 °C for 1 h until the formation of stable sol. The methodology for preparation of stock solution was discussed in our earlier reports [18]. Before deposition of thin film, platinized silicon (Pt(111)/Ti/SiO₂/Si) substrate was thoroughly cleaned with detergent solution and washed using de-ionized (DI) water. Afterward, ultrasonication was carried out in presence of acetone, methanol, 2-propanol and DI water for 5 min in each. A drop of stock solution was placed on Pt–Si substrate, and then, the solution was coated uniformly by means of spin-coating technique at a speed of 3000 rpm for 30 s. After, the wet film was pre-baked by keeping in a hot plate at 200 °C for 5 min. This process for coating and heating cycle was repeated for 9 times to attain the desired thickness of $(\text{BiFeO}_3)_x$ – $(\text{BiCrO}_3)_{1-x}$ thin layer. Finally, the amorphous films were pyrolyzed at 400 °C for 30 min in muffle furnace for removing of organic residuals.

The structures of the films were examined by X-ray diffraction (XPERT PRO X-ray diffractometer) with the CuK_α radiations ($\lambda = 1.5406 \text{ \AA}$). Morphological characterization was performed using scanning electron microscope (SEM, Hitachi, S-4700, Japan) and atomic force microscope (AFM) (Park system, XE-70, Netherland). The frequency dependence of dielectric behavior was measured in the frequency range from 10^2 to 10^5 Hz using LCRQ meter (Aplab, 5200). The magnetic (M–H curve) measurements were carried out with Lake Shore 7410 vibrating sample magnetometer (VSM). Ferroelectric (P–E) hysteresis loop, positive up and negative down (PUND) and leakage current (J–V) measurements were carried out by using M/s Radiant Premier-II system, USA. All these electrical characterization was carried out at room temperature.

3 Results and Discussion

3.1 XRD Analysis

The X-ray diffraction (XRD) patterns of the $(\text{BiFeO}_3)_x-(\text{BiCrO}_3)_{1-x}$ composite thin films on Pt (111)/Ti/SiO₂/Si substrate crystallized at 400 °C are shown in Fig. 1. It can be seen that pure BFO and BCO thick films have a single phase of rhombohedral and tetragonal structures for $x = 0$ and 1, respectively. There are two phases such as BiFeO_3 and BiCrO_3 distinctly identified in the intermediate composition for $x = 0.25$ and 0.75. The intensity of the diffraction peaks is dependent on the amount of the

corresponding phase. The amount of phase fraction present in the composite materials is measured and their preferential orientation peak intensity are calculated using some relation is as follows,

$$\text{Phase fraction of BFO} = \frac{(110)I_{\text{BFO}}}{(211)I_{\text{BCO}} + (110)I_{\text{BFO}}} \quad (1)$$

$$\text{Phase fraction of BCO} = \frac{(211)I_{\text{BCO}}}{(110)I_{\text{BFO}} + (211)I_{\text{BCO}}} \quad (2)$$

The obtained phase fractions are closely related to those of stoichiometry of even a single constituent body, which can be observed from Table 1 confirming the formation of a composite material without measurable interdiffusion. Within the resolution limit of the XRD equipment, no other phases were detected, confirming the successful preparation of dual-phase composite materials in this system. Compared to the previous report [21], the recent study had a higher purity under lower annealing temperature. With the increase in the x ($x > 0.05$) value, major diffraction peaks shifting toward the lower diffraction originate from the lattice distortion due to their difference in ionic radius between Cr^{3+} (0.615 Å) and Fe^{3+} (0.645 Å).

3.2 Morphological Studies

3.2.1 Scanning Electron Microscopy (SEM)

Figure 2 shows the typical morphological images of $(\text{BiFeO}_3)_x-(\text{BiCrO}_3)_{1-x}$ composite thin film. It clearly demonstrates that the film is composed of flat and rough regions showing a porous and honey comb-like structure with well-distributed grains. It can be seen that each pore is surrounded by the walls with some apertures (small opening) in the entire surface at all films. The most homogenous pore distribution is observed when the BFO addition is $x = 0.25$, while the pore size is not so uniform and larger pores as well as agglomerated particles occur in other cases. The further higher BFO addition ($x = 0.75$), working as a pore-forming agent, suppresses the driving force of densification without affecting the connections of neighboring grains while excessive BFO amount would lead to the collapse of the porous structure and thus increase the porous width.

Table 1 Calculated phase fraction of $(\text{BiFeO}_3)_x-(\text{BiCrO}_3)_{1-x}$ composites at $x = 0, 0.25, 0.75$ and 1

Composition	Phase fraction for BFO–BCO composites	
	Phase I (BFO)	Phase II (BCO)
$x = 0$	–	100
$x = 0.25$	29.2	70.8
$x = 0.75$	71.5	28.5
$x = 1$	100	–

Fig. 1 X-ray diffraction patterns for $(\text{BiFeO}_3)_x-(\text{BiCrO}_3)_{1-x}$ thin films at $x = 0, 0.25, 0.75$ and 1 over Pt(111)/Ti/SiO₂/Si substrate at 400 °C

Fig. 2 SEM/EDAX for $(\text{BiFeO}_3)_x-(\text{BiCrO}_3)_{1-x}$ thin films at $x = 0$ **a**, 0.25 **b**, 0.75 **c**, 1 **d** on Pt(111)/Ti/SiO₂/Si substrate

Obviously, excessive BFO ($x = 1.0$) would lead to the collapse of the porous structure and therefore the opposite tendency of porous width and linear shrinkage is observed. The porous size and surface profile parameter for composition $(\text{BiFeO}_3)_x-(\text{BiCrO}_3)_{1-x}$ where $x = 0, 0.25, 0.75$ and 1 is summarized in Table 2. In order to provide further evidence to support the above assumption, we investigate roughness (R_q) using atomic force microscope.

3.2.2 Surface Topography (AFM)

The crystalline arrangement and surface topography of the films under different doping concentrations were studied

Table 2 Relationship between pore size and roughness (R_q) for all composition

Composition	Pore size (nm)	Roughness (R_q)
0	450	6.523
0.25	230	14.157
0.75	110	18.544
1	420	9.095

using atomic force microscope (AFM). Figure 3 describes the granular nature and roughness of the coated film at time of contact with cantilever. Hence, the obtained roughnesses are well sufficient to carry out electrical and magnetic studies. The peaks in Fig. 4 were found to be broad,

Fig. 3 Image showing the coarse surface of the film before scanning by the AFM cantilever

showing that the obtained films were nanostructured with even distribution. The average crystalline sizes estimated from Scherrer formula undergo correlation with the above AFM image, and the average peaks size differs, i.e., the peaks size gets increased with the effect of increasing concentration. The roughness obtained from AFM was already compared with the porous size of SEM in Table 2 for the reliability in studying magnetic and electrical properties.

3.3 Magnetic Hysteresis (M–H) behavior at different compositions of $(\text{BiFeO}_3)_x-(\text{BiCrO}_3)_{1-x}$ Thin Films

Field dependence of magnetization at room temperature for $(\text{BiFeO}_3)_x-(\text{BiCrO}_3)_{1-x}$ thin films is shown in Fig. 5. When comparing with the phase of BFO and BCO thin films, the remnant magnetization and coercive magnetic field values for the BCO/BFO composites are relatively larger with clear hysteresis. The observed weak ferromagnetism might be attributed to $\text{Fe}^{3+}-\text{Cr}^{3+}$ interactions and the suppression of the spin inhomogeneity of the BFO in the BCO/BFO double-layered thin film. The observed electrical and

multiferroic properties of the composite thin films are correlated with net effects, such as the decrease in oxygen vacancy density. The reason for suppression of spin in homogeneity is due to the stabilization of the perovskite structure, small changes in the lattice parameter caused by lattice mismatching and compressive strain caused by coupling of the BFO and BCO layers [10]. For two composites, $x = 0.75$ expose higher magnetization with a saturated magnetization of 9.868×10^{-4} emu and with a remnant magnetization of 2.167×10^{-5} emu, which indicates Cr^{3+} doping could be helpful in increasing the magnetic moment. However, the Cr might give rise to a change in anisotropy constant by driving the transition from a modulated spin structure to homogeneous due to size difference between Cr^{3+} and Fe^{3+} .

3.4 Electric Behavior of $(\text{BiFeO}_3)_x-(\text{BiCrO}_3)_{1-x}$ Thin Films

The frequency dependence of dielectric constant ϵ_r of the thin film is shown in Fig. 6. Results reveal that the dielectric constant decreases with increasing frequency for all four samples. The decrease in dielectric constant is

Fig. 4 3D AFM image for $(\text{BiFeO}_3)_x-(\text{BiCrO}_3)_{1-x}$ thin films at $x = 0$ **a**, 0.25 **b**, 0.75 **c**, 1 **d** on Pt(111)/Ti/SiO₂/Si substrate

Fig. 5 **a** M–H loop for $(\text{BiFeO}_3)_x-(\text{BiCrO}_3)_{1-x}$ thin films at $x = 0, 0.25, 0.75$ and 1 over Pt(111)/Ti/SiO₂/Si substrate. **b** Zoom plot of M–H loop for $(\text{BiFeO}_3)_x-(\text{BiCrO}_3)_{1-x}$ at $x = 0$ and 1

mainly attributed to the mismatch of interfacial polarization of the composites to external electric field at elevated frequencies. As expected, the variation tendency of dielectric constant with frequency is the reverse of electrical conductivity [22]. It is because, as mentioned above, the influence of frequency prevails or the dipolar polarizations of the composites lose the response to electric fields in the high-frequency region and the analyzed value in this region. The observed reduction in the dielectric constant at high-frequency region is attributed to the reduced contribution of space charge polarization resulting from the presence of the BCO layer and suggests a lower oxygen vacancy concentration in BCO–BFO thin film [10]. Accordingly, the change in dielectric constant for the composite $(\text{BiFeO}_3)_x-(\text{BiCrO}_3)_{1-x}$ shows much more

dependent at increasing x values from 0 to 0.75 in the tested frequency region and showed a larger dielectric constant for 0.75 than that of other composition at $0, 0.25$ and 1 . The permittivity increase dramatically near the percolation threshold for $x = 0.75$ indicates the growth in large number of dipoles, that may be due to predominance of Fe^{3+} than Cr^{3+} by causing interfacial defects. Therefore, the peaks get shifted to higher frequency resulting with an increase in peak height during the increase of substitution of Cr^{3+} ions. This causes decrease in distance between the ions and results in changing of hopping frequency [23]. As a result of the increase in polarization, the dielectric constant gets increase. However, above and below in the percolation threshold, the ions and electrons are less oriented toward the field direction and hence the dielectric constant gets decrease.

Fig. 6 Dielectric constant for $(\text{BiFeO}_3)_x-(\text{BiCrO}_3)_{1-x}$ thin films at $x = 0, 0.25, 0.75$ and 1 over Pt(111)/Ti/SiO₂/Si substrate

The dielectric loss ($\tan \delta$) versus frequency curves of the composite thin film for all the samples are shown in Fig. 7. The relaxation peak for all the samples appears to be dominating at the low-frequency region from 0.1 to 1 kHz. Occurrence of dielectric loss peak is due to the probability of ion exchange between the two states, i.e., natural frequency jump between the two positions and the external applied alternating electric field frequency matches; maximum electrical energy is transferred to the oscillating ions and power loss shoots up, thereby resulting in resonance which is in agreement with Debye relaxation theory. The relaxation peak is found to shift toward higher-frequency side with the increase in x values; Fe^{3+} prefers B-site which strengthens the dipole–dipole interaction leading to hindrance to the rotation of the dipoles. High loss in pure phases is due to existence of more free charge carriers or more oxygen vacancies within the film. With the increase in the x value, the free charge carrier's present get arrested,

Fig. 7 Dielectric loss for $(\text{BiFeO}_3)_x-(\text{BiCrO}_3)_{1-x}$ thin films at $x = 0, 0.25, 0.75$ and 1 over $\text{Pt}(111)/\text{Ti}/\text{SiO}_2/\text{Si}$ substrate

i.e., the charge carriers find difficult to transport, leading to reduction in loss. Similar low value of dielectric loss was found in higher-order incorporation of 0.75 into the composite materials. Alternatively, the higher dielectric constant and low loss mainly originate from its less porosity. This also indicates that decreasing dielectric constant was the increase in porosity. Two phases 0 and 1 form more porous structures which results in hopping of electrons causing the increase in electrical conduction [24]. The first and main reason is that due to the volatilization of more Bi in BFO and BCO structures during annealing process, while for 0.25 and 0.75, the valence occupancy gets occupied during substitution of ions.

Polarization vs electric field characteristics of the BCO/BFO composite thin film were measured under a maximum applied field from -20 to 20 kV/cm and are shown in Fig. 8. For every compositional doping, the values of coercivity and polarization are changed. The remnant polarization (P_r) and coercivity (E_c) changes with the x value indicate the atomic disorderness in structure, and presence of large leakage arises within the materials. The pure phase of BCO and BFO shows an optimized ferroelectricity property with minimal values of P_r and E_c , which may be due to intrinsic nature of large leakage current and domain switching. For BCO, BFO, $\text{BFO}_{0.25}$ -BCO $_{0.75}$ and $\text{BFO}_{0.75}$ -BCO $_{0.25}$, the remnant polarization ($\mu\text{C}/\text{cm}^2$) values are found to be 2.413, 4.157, 6.268 and 9.11, respectively, and the corresponding coercivity (kV/cm) values are 5.853, 7.068, 8.881 and 10.69, respectively. Comparatively large polarization values were recorded for the BCO/BFO composite thin film, as opposed to those of the BFO and BCO thin film, which confirmed the enhanced ferroelectric properties of the

Fig. 8 P-E loop for $(\text{BiFeO}_3)_x-(\text{BiCrO}_3)_{1-x}$ thin films at $x = 0, 0.25, 0.75$ and 1 over $\text{Pt}(111)/\text{Ti}/\text{SiO}_2/\text{Si}$ substrate

composite film. Hence, decreased grain size in pure phase causes an extrinsic effect (grain size effect) for weakened ferroelectric, wherein small grain size means large amount of grain boundary, which leads to polarization discontinuity between grains and hence decreases polarization. This might be related to a decrease in the number of oxygen vacancies in which ferroelectric thin films are known to be mobile charges that play a key role in conduction, in turn increasing the leakage current density and reduce remnant polarization [25]. Judging from the P-E loops, the sample is relatively leaky; therefore, positive up and negative down (PUND) measurement was carried out. The film undergoes five identical pulses with equal magnitude and width during the performance of PUND (Fig. 9) analysis. The first pulse presets the polarization state of a ferroelectric sample to a given direction. The second pulse switches the sample to the opposite state, and the switched polarization value is extracted. A second non-switching measurement is performed by applying the third pulse identical to the second one after it returns to zero volts and a programmable delay period passes. The fourth and fifth pulses mirror the second and third pulses, but point in the opposite direction [26]. From these curves, the ferroelectric domain observation, domain switching behavior and the switchable polarization were detected and confirmed the ferroelectric property of the BFO/BCO film. The E_c values in all films remain unchanged and therefore, switched charge ferroelectric density (Q_{sw}) in Fig. 9 showed slighter modification with increasing of x values from 0 to 0.75 values. The obtained switched charge polarization ($Q_{sw} = 10 \mu\text{C}/\text{cm}^2$ at a pulse width of 0.1 ms) for 0.75 compositions agrees well with the P-E hysteresis loop measurement at Fig. 8. Thus, it can be concluded that the BFO film with an $x = 0.75$ compositions has an ideal ferroelectric behavior among all films. Figure 10

Fig. 9 PUND measurement for $(\text{BiFeO}_3)_x-(\text{BiCrO}_3)_{1-x}$ thin films at $x = 0, 0.25, 0.75$ and 1 over $\text{Pt}(111)/\text{Ti}/\text{SiO}_2/\text{Si}$ substrate. *Inset* shows the plot variation between switched charge density (Q_{sw}) and BFO/BCO doping

illustrates the leakage current density (J) versus applied electric field (E) plots of the BCO/BFO thin film. It shows that the leakage currents of $\text{BiFe}_{0.25}\text{Cr}_{0.75}\text{O}_3$ and $\text{BiFe}_{0.75}\text{Cr}_{0.25}\text{O}_3$ get decreased by two to three orders of magnitude compare to the pure BFO ($x = 1$) and BCO ($x = 0$) thin films. For pure phases a substantial number of oxygen vacancies like Fe^{3+} and Cr^{3+} are created to compensate the positive charge deficiency caused by the loss of “Bi” during annealing. Among these films, BFO displays the higher dielectric loss (0.91 at 1 kHz), which is correlated to Bi deficiency, oxygen vacancies, valence fluctuation of the Fe ($\text{Fe}^{2+}/\text{Fe}^{3+}$) ion and poor microstructure. The low value of leakage current in dual-phase thin films is associated with two aspects

Fig. 10 J-E versus electric field for $(\text{BiFeO}_3)_x-(\text{BiCrO}_3)_{1-x}$ thin films at $x = 0, 0.25, 0.75$ and 1 over $\text{Pt}(111)/\text{Ti}/\text{SiO}_2/\text{Si}$ substrate

(a) structural transformation (the coexistence structure of tetragonal and rhombohedral structure) and (b) creation of oxygen vacancies (presence of extra valence ions). Also, it is obvious that the insulating BCO layer is able to act as a barrier to prevent the flow of charge carriers in the BCO/BFO double-layered thin film [10] indicating that the BCO layer reduced the defects at the interface. During the nucleation and early growth of the films, a poor heterogeneous nucleation with a low density of critical nucleus facing a weak incoming shower of bismuth ferrite would promote growth of porous and rough layers. Compared with the dense and smooth surfaces 0.25 and 0.75 films, the more porous and rougher surfaces of the $x = 0$ and 1 films can open up more conducting channels under the same electric field, resulting in larger leakage currents and higher dielectric loss. As shown in Fig. 10 a plot of $\log(J)$ against $\log(E)$ is found linear with a slope value of $S \sim 1$ over the entire region over the applied, which can be further related to Ohmic conduction mechanism [27].

4 Conclusion

High-quality thin films of $(\text{BiFeO}_3)_x-(\text{BiCrO}_3)_{1-x}$ on $\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$ substrate were prepared by sol-gel method. SEM and AFM images showed the formation of uniform porous structures with increase and decrease in grain boundaries for different compositions at $x = 0, 0.25, 0.75$ and 1 . In addition, the pore size and surface parameters were interrelated for all compositions. The effect of dielectric and multiferroic properties of $(\text{BiFeO}_3)_x-(\text{BiCrO}_3)_{1-x}$ are varied with the effect of porous nature and size of the films. Among all compositions of $(\text{BiFeO}_3)_x-(\text{BiCrO}_3)_{1-x}$, 0.75 compositions shows superior behavior than 0.25 and showed improved ferromagnetic and ferroelectric behaviors compared with those of the pure and end phase. This obvious behavior of 0.75 compositions is due to $\text{Fe}^{3+} < > \text{Cr}^{3+}$ super-exchange interaction with 180° exchange mechanism. The initial results obtained are thus quite satisfactory and hence stand as a future application for nonvolatile Fe-RAM applications due to its less ordered leakage current under well-saturated ferroelectric behavior with enhanced magnetization field. All these properties undergo cumulating to provide good recommended memory applications in upcoming research technology as a good memory device for spintronics.

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References

- [1] B. Razavi, *IEEE J. Solid State Circuits* **32**, 5 (1997)
- [2] H. Nwe, Y. Maung, T. Win, K. Soe, *Adv. Mater. Res.* **557**, 1861–1864 (2012)
- [3] N. Ortega, A. Kumar, J.F. Scott, R.S. Katiyar, *J. Phys.: Condens. Matter* **27**, 504002 (2015)
- [4] S.K. Singh, K. Sato, K. Maruyama, H. Ishiwara, *Jpn. J. Appl. Phys.* **45**, 37–41 (2006)
- [5] S.K. Singh, R. Ueno, H. Funakubo, H. Uchida, S. Koda, H. Ishiwara, *Jpn. J. Appl. Phys.* **44**, 23–28 (2007)
- [6] S.K. Singh, S. Shanthi, H. Ishiwara, *J. Appl. Phys.* **108**, 054102 (2010)
- [7] Y. Zhang, S. Yu, J. Cheng, *J. Eur. Ceramic Soc.* **30**, 271–275 (2010)
- [8] N.A. Hill, P. Bättig, C. Daul, *J. Phys. Chem B* **106**, 3383–3388 (2002)
- [9] D.H. Kim, H.N. Lee, M. Varela, H.M. Christen, *J. Appl. Phys.* **89**, 162904 (2006)
- [10] J.W. Kim, C.M. Raghavan, J.-W. Kim, S.S. Kim, *Ceram. Int.* **41**, 7211–7215 (2015)
- [11] B.R. Kumar, T. Subba Rao, *Digest J. Nanomater. Biostruct.* **7**, 1881–1889 (2012)
- [12] L.W. Martin, D.G. Schlom, *Curr. Opin. Solid State Mater. Sci.* **16**, 199–215 (2012)
- [13] P. Meenakshi, R. Karthick, M. Selvaraj, S. Ramu, *Solar Energy Mater. Solar Cells* **128**, 264–269 (2014)
- [14] B.N. Dash, P. Mallick, R. Biswal, J. Prakash, A. Tripathi, D. Kanjilal, N.C. Mishra, *Bull. Mater. Sci.* **36**, 813–818 (2013)
- [15] R. Nechache, C. Harnagea, A. Rudeiger, F. Rosei, A. Pignoletm, *Funct. Mater. Lett.* **3**, 83 (2010)
- [16] H.W. Jang, S.H. Baek, D. Ortiz, C.M. Folkman, C.B. Eom, Y.H. Chu, P. Shafer, R. Ramesh, V. Vaithyanathan, D.G. Schlom, *Appl. Phys. Lett.* **92**, 062910 (2008)
- [17] J. Li, J. Wang, M. Wuttig, R. Ramesh, N. Wang, B. Ruetter, A.P. Pyatakov, A.K. Zvezdin, D. Viehland, *Appl. Phys. Lett.* **84**, 526 (2004)
- [18] R.V. William, A. Marikani, D. Madhavan, *Ceram. Int.* **42**, 6807–6816 (2016)
- [19] L.B. Cheng, C. Chang, X. Zhi, X. Qian, *Phys. Lett. A* **374**, 4265–4268 (2010)
- [20] R. Nechache, F. Rosei, *J. Solid State Chem.* **189**, 13–20 (2012)
- [21] P. Thiruramanathan, A. Marikani, D. Madhavan, K. Gangatharan, *Trans. Indian Inst. Met.* (2016). doi:[10.1007/s12666-016-0845-4](https://doi.org/10.1007/s12666-016-0845-4)
- [22] Y. Chao Li, R. Kwok, Y. Li, S. Chin Tjong, *J. Nanomater.* **10**, 261748 (2010)
- [23] K.M. Nair, D. Suvorov, R.W. Schwartz, R. Guo, *Advances in Electroceramic Materials*, 1st edn. (Wiley, Hoboken, 2009), p. 162
- [24] C. Wang, M. Takahashi, H. Fujino, X. Zhao, E. Kume, T. Horiuchi, S. Sakai, *J. Appl. Phys.* **99**, 054104 (2006)
- [25] H. Li, J. Zhu, J. Zhuang, Y. Hu, M. Huai, Q. Yang, *J. Sol–Gel Sci. Technol.* (2015). doi:[10.1007/s10971-015-3706-4](https://doi.org/10.1007/s10971-015-3706-4)
- [26] X.J. Lou, J. Wang, *J. Appl. Phys.* **108**, 034104 (2010)
- [27] J. Wu, J. Wang, D. Xiao, J. Zhu, *J. Appl. Phys.* **109**, 124118 (2011)