Dielectric properties of $\text{BaMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ doped $\text{Ba}_{0.45}\text{Sr}_{0.55}\text{TiO}_3$ thin films for tunable microwave applications

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$\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (BMN) doped and undoped $\text{Ba}_{0.45}\text{Sr}_{0.55}\text{TiO}_3$ (BST) thin films were deposited via radio frequency magnetron sputtering on $\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Al}_2\text{O}_3$ substrates. The surface morphology and chemical state analyses of the films have shown that the BMN doped BST film has a smoother surface with reduced oxygen vacancy, resulting in an improved insulating properties of the BST film. Dielectric tunability, loss, and leakage current (LC) of the undoped and BMN doped BST thin films were studied. The BMN dopant has remarkably reduced the dielectric loss ($\sim 38\%$) with no significant effect on the tunability of the BST film, leading to an increase in figure of merit (FOM). This is attributed to the opposing behavior of large Mg^{2+} whose detrimental effect on tunability is partially compensated by small Nb^{5+} as the two substitute Ti^{4+} in the BST. The coupling between Mg_{Ti}'' and $\text{V}_{\text{O}}^\bullet$ charged defects suppresses the dielectric loss in the film by cutting electrons from hopping between Ti ions. The LC of the films was investigated in the temperature range of 300–450 K. A reduced LC measured for the BMN doped BST film was correlated to the formation of defect dipoles from Mg_{Ti}'' , $\text{V}_{\text{O}}^\bullet$ and $\text{Nb}_{\text{Ti}}^\bullet$ charged defects. The carrier transport properties of the films were analyzed in light of Schottky thermionic emission (SE) and Poole–Frenkel (PF) emission mechanisms. The result indicated that while the carrier transport mechanism in the undoped film is interface limited (SE), the conduction in the BMN doped film was dominated by bulk processes (PF). The change of the conduction mechanism from SE to PF as a result of BMN doping is attributed to the presence of uncoupled $\text{Nb}_{\text{Ti}}^\bullet$ sitting as a positive trap center at the shallow donor level of the BST.

Keywords: Barium strontium titanate; sputtering; ferroelectric thin film; tunability; leakage current; permittivity; loss; figure of merit; defect dipole.

1. Introduction

Barium strontium titanate (BST) thin films have been applied for tunable microwave devices such as phase shifters, delay lines, and filters¹ due to the DC field dependence of its dielectric constant. Large tunability accompanied by low dielectric loss is vital for the application of BST films in the tunable microwave components.^{1,2} However, attaining both in parallel remains to be a challenge since large tunability is often followed by high dielectric loss and vice versa.³

Numerous studies have shown that incorporating small amount of aliovalent (e.g., Mg^{2+} ⁴, La^{3+} ⁵, Al^{3+} ⁶, Ce^{3+} ⁷, Nb^{5+} ^{6,8}) or isovalent (e.g., Zr^{4+} , Sn^{4+} , Ge^{4+} ⁹) ions into a BST lattice effectively modifies the dielectric properties (tunability, dielectric loss, and leakage current (LC)) of the BST film.¹⁰ Mg^{2+} and Nb^{5+} , which are acting as an electron acceptor and donor, respectively, by replacing the B site of the $(\text{A}^{2+}\text{B}^{4+}\text{O}_3^{2-})$ perovskite, have received the most attention because of their drastic effect in altering the dielectric properties of the BST film.^{4,6,8,11–14} Individually, each ion improves either the tunability or the insulating properties of

BST — not both at a time. Adding Mg^{2+} ($\sim 1\text{--}5\text{ mol}\%$) suppresses the dielectric loss and the LC; but, these come with a huge drop in dielectric constant and tunability of the BST film.^{4,11} Conversely, doping BST with Nb^{5+} ($\sim 5\text{ mol}\%$) increases the dielectric constant and tunability;^{8,12,15} however, these are accompanied by the increase of dielectric loss and LC, mainly due to the excess electron that Nb donates when it substitutes Ti site.^{6,13,14}

Doping BST with Mg^{2+} and Nb^{5+} concomitantly may improve both the tunability and insulating properties of BST. One of the few studies in this area has shown that the LC was reduced to a minimum when a metalorganic deposited BST films is co-doped with Mg and Nb at the donor/acceptor compensated concentration.¹⁶ Similarly, introducing $\text{BaMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (BMN), contains both Mg and Nb, into BaTiO_3 (BTO) has significantly increased its dielectric constant.^{17–19} BMN, by itself, is a complex perovskite oxide which exhibit high dielectric constant, low dielectric loss, and small temperature coefficient making it a material of interest for communication satellite and radar detector applications.²⁰

When used as a dopant, it ensures the total charge neutrality (realized when $[\text{Mg}_{\text{Ti}}''] = 2[\text{Nb}_{\text{Ti}}^{\bullet}]$) which is desirable to obtain a minimum LC in the BST film.^{16,21} In the present work, we report on the effects of the BMN dopant on the surface chemical state, LC, transport mechanisms, and figure of merit (FOM) — tread-off between tunability and dielectric loss — of the BST film. The conduction mechanism in the undoped and BMN doped BST films was analyzed in light of the Schottky thermionic (SE) and Poole–Frenkel (PF) emission mechanisms. We found that the carrier transport in the undoped film is interface limited while the doped one is bulk limited. The shift of the carrier transport from interface to bulk limited mechanism is associated to the presence of positive trap centers due to Nb ion sitting at the shallow donor level of BST.

2. Experiment

BMN (4 mol%) doped and undoped BST thin films were deposited via radiofrequency (RF) magnetron sputtering (CMS-18 Kurt J. Lesker) in an oxygen environment on Pt/TiO₂/SiO₂/Al₂O₃ substrates (on semiconductor) from the respective sputtering targets. Detailed procedures for the fabrication of the doped and undoped BST sputtering targets are presented elsewhere.²¹ For the sputter deposition of both films, the base pressure, throw distance, substrate temperature, and RF power were set to 2×10^{-8} Torr, 16.5 cm, 700°C, and 150 W (or 3.3 W/cm² power density), respectively. The Ar and O₂ gas compositions were 60 sccm and 40 sccm, respectively, with the total gas pressure in the chamber of 5 mTorr. To improve the BST film crystallinity, a self-buffer layer (~10 nm) was deposited on the substrates at room temperature followed by increasing the temperature to a set value of 700°C (at ~15°C/min), at which the main body of the film was deposited. The thickness of both films, measured with an ellipsometer (J. A. Woollam, M88), was about 250 nm. Atomic force microscopy (AFM, Veeco dimension 3100) was used to evaluate the surface morphology and film roughness. The chemical composition and valance state of the deposited BST thin films were examined by X-ray photoelectron spectroscopy (XPS) using K-alpha spectrometer from ThermoFisher Scientific with hemispheric detector and monochromatic AlK α ($h\nu = 1486.6$ eV) radiation. The system is equipped with a low voltage electron flood gun to compensate the charging effect that causes shift in the binding energy. The dielectric and electrical properties were measured in a metal–insulator–metal (MIM) capacitor structure using 500 nm sputter deposited Pt top electrode. Prior to depositing the Pt top electrode, the films were annealed at 400°C at ambient pressure under the flow of oxygen (10 sccm) for 1 h to remove water and organic molecules from their surfaces. Then, the films were lithographically patterned and ion milled to devices consisting of two 0.5×0.5 mm² top electrodes separated by 0.2 mm gap (equivalent to two capacitors

connected in series). To repair the ion milling damages, the films were annealed at 650°C in oxygen flow (15 sccm) after stripping the photoresist by oxygen plasma. The measurement of capacitance–voltage ($C-V$) and loss tangent–voltage ($\tan \delta-V$) were performed by Cascade Microtech Summit 12000 Semi-Automatic Wafer Prober equipped with Agilent E4991A RF impedance analyzer at a frequency of 30 MHz. Keithley 6487 Picoammeter/Voltage Source was used to apply an external bias. The LC dependence on the applied voltage and temperature was measured by Agilent B1500A Semiconductor Device Analyzer by using a hotplate whose temperature was monitored by an external thermocouple.

3. Results and Discussions

3.1. Surface morphology and chemical state of the films

Figure 1 shows the 2D AFM images of both undoped BST (A) and BMN doped BST (B) films taken from scan area of 1×1 μm^2 . The film surface morphology may considerably alter the quality of the electrode–film interface and thus affect the tunable device performance. Both films exhibit dense

Fig. 1. 2D AFM images of undoped BST (a) and BMN doped BST (b) films deposited on Pt/TiO₂/SiO₂/Al₂O₃ substrates.

crystalline microstructure, without visible cracks, pinholes or other defects. However, the AFM images demonstrated that doping has appreciably suppressed the film surface roughness reducing it from 7 nm for undoped BST down to 5 nm ($\sim 28\%$ reduction).

It is also evident from the AFM images (Figs. 1(a) and 1(b)) that the BMN doped film has a smaller grain sizes presumably due to a pinning effect on the grain boundaries that hinders the grain growth. A similar grain inhibition effect was also observed in Nb and Mg doped BST films.^{16,21,22} The reduced surface roughness in the BMN doped film is consistent with smaller grain size and is essential to minimize the LC or increase film resistivity,^{22,23} which is in accord with our findings (vide infra).

Surface chemical properties of the films were studied by XPS in which Ba, Sr, Ti, and O elements were detected on the XPS survey scan for both films (data not shown). The detailed XPS analysis will be reported elsewhere, but here we focus on the Ba3d core levels for comparison of the chemical states of the two films. Figures 2(a)–2(c) present the narrow XPS scan showing the core levels of Ba3d, Nb3d, and Mg1s. As expected from doping, the Mg and Nb species are only present in the BMN doped BST film.

The Ba3d peaks for both films are composed of XPS lines corresponding to $Ba3d_{3/2}$ and $Ba3d_{5/2}$ spin-orbit coupling pairs positioned at higher and lower binding energies, respectively. Each line shape has two clearly visible components which are deconvoluted using Gaussian fit as indicated in the figure. For the undoped film, the Ba3d peaks were decomposed into symmetric Gaussian components that are centered at 778.4 eV and 779.9 eV for $Ba3d_{5/2}$ and 793.8 eV and 795.3 eV for $Ba3d_{3/2}$. Similarly for the doped film, the fitting has resulted in components that are peaked at 778.8 eV and 780.2 eV for $Ba3d_{5/2}$ and 794.2 eV and 795.6 eV for

$Ba3d_{3/2}$. These two peaks are often reported in the literature, with the components at the lower and higher binding energies known as alpha (α) and beta (β) phases (see Fig. 2(a)), respectively.^{24–28} The α -phase is associated to Ba atoms in BST perovskite²⁴ while the β -phase is coupled with Ba atom in BST nonperovskite environment, such as carbonates,²⁷ oxides,²⁸ and relaxed BST phases due to oxygen vacancy and residual defects.^{24,26} Moreover, in Ref. 25 after performing XPS analysis at variable emission angles, the β -phase was found to be Ti-poor, Ba and Sr rich nonperovskite structure dominant on the surface of the film than the bulk.

Using the Gaussian peak area (A) from the fit, the fraction of the β -phase ($= A(\beta)/(A(\alpha) + A(\beta))$), is estimated to be 0.55 for the undoped film and 0.52 for the doped one, indicating that the very top surface of both films is populated dominantly with nonperovskite phase, which could be attributed to the presence of oxygen vacancy.²¹ Though insignificant, the higher β -phase fraction for undoped film shows a Ti poor surface as well as higher oxygen vacancy which exhibits itself through the increase of dielectric loss and LC.^{26,29,30} On the other hand, the peak positions for the undoped film $\alpha(Ba3d_{5/2}, Ba3d_{3/2})$ and $\beta(Ba3d_{5/2}, Ba3d_{3/2})$ are comparable with what has been reported by others,^{24–28} but the doping has introduced a surface core level shift towards higher binding energy by about 0.4 eV. The spin-orbit coupling distance $\alpha(Ba3d_{5/2} \rightarrow Ba3d_{3/2})$ and $\beta(Ba3d_{5/2} \rightarrow Ba3d_{3/2})$ for both films was 15.4 eV which is consistent with the reported results,²⁴ indicating that the chemical valance of Ba in both films as well as the observed phases is +2.

3.2. Effect of BMN dopant on the LC of BST film

Figure 3 shows the LC versus voltage graphs of the undoped (Fig. 3(a)) and BMN doped (Fig. 3(b)) BST thin films in a

Fig. 2. (Color online) Narrow scan XPS spectra of Ba3d (a), Mg1s (b), and Nb3d (c) for the undoped and BMN doped BST thin films. The black and red lines in (b) and (c) are indicating the spectrum from the undoped and BMN doped samples, respectively.

Fig. 3. Variable temperature (300–450 K) current voltage (IV) characteristics of the undoped (a) and BMN doped (b) BST thin films deposited on Pt/TiO₂/SiO₂/Al₂O₃ substrates.

temperature range of 300–450 K. The LC measured for the BMN doped film is lower than the undoped film, suggesting that the Mg/Nb co-doping (through BMN) that ensures the charge neutrality compensation (i.e., $[\text{Mg}_{\text{Ti}}''] = 2[\text{Nb}_{\text{Ti}}^{\bullet}]$) reduces the LC of the BST film.^{16,21} As can be seen from the figure, the LC for each film has shown strong dependence on temperature and presents two voltage regimes. In the low voltage regime, the LC is insignificant and remains nearly constant with voltage. However, beyond certain minimum bias voltage, the LC rises exponentially. This minimum bias voltage above which the BST capacitor leaks appreciably is observed to decrease (see the left shifting of the $I-V$ profiles) with temperature for both films, essentially, due to the increase of free carrier concentration resulting from thermal excitation. Interestingly, the BMN doped film requires higher voltage (>10 V) compared with the undoped BST film to allow substantial increase of LC, confirming the improvement of the insulating properties of BST with the dopant. This imply that higher control voltage can be applied to tune the capacitance of a device made of the BMN doped BST film without triggering major dielectric losses.²

The doping behavior of BMN in BST can be presented by a defect reaction (Kroger–Vink notation) scheme shown in Eq. (1)³¹

This reaction scheme illustrates when Mg^{2+} and Nb^{5+} substitute Ti^{4+} , they form Mg_{Ti}'' and $\text{Nb}_{\text{Ti}}^{\bullet}$ charged defects due to the difference between the valance state of the dopants and the titanium ion. In addition to these extrinsic charged defects, the missing of oxygen from its crystallographic site (revealed by XPS) forms an intrinsic charged defect, oxygen vacancy ($\text{V}_{\text{O}}^{\bullet\bullet}$)^{21,30} which can be written as in Eq. (2):

These charged defects are generally responsible for increasing the total electrostatic energy of the crystal. However, it is well documented that when oppositely charged defects are incorporated into a ferroelectric crystal they form defect dipoles in order to minimize the total electrostatic energy of the crystal.^{16,32,33}

In our case, owing to the presence of two donor defects ($\text{Nb}_{\text{Ti}}^{\bullet}$ and $\text{V}_{\text{O}}^{\bullet\bullet}$) and one acceptor defect (Mg_{Ti}''), two types of defect dipoles may be formed as $(\text{Mg}_{\text{Ti}}'' \rightarrow 2\text{Nb}_{\text{Ti}}^{\bullet})$ ¹⁶ and $(\text{Mg}_{\text{Ti}}'' \rightarrow \text{V}_{\text{O}}^{\bullet\bullet})$.³² These defect dipoles act as insulating layers or enhance the potential barriers of BST and thus reduce the LC in the film. Moreover, in this work, the relationship between the concentration of Mg and Nb is pre-adjusted to satisfy the neutrality condition in the BST crystal (i.e., $[\text{Mg}_{\text{Ti}}''] = 2[\text{Nb}_{\text{Ti}}^{\bullet}]$), implying that every Mg_{Ti}'' is coupled with $\text{Nb}_{\text{Ti}}^{\bullet}$. However, owing to the small distance between the sites of Mg_{Ti}'' and $\text{V}_{\text{O}}^{\bullet\bullet}$ ($\sim 1.975\text{\AA}$) in the BST perovskite structure, the coupling between Mg_{Ti}'' and $\text{V}_{\text{O}}^{\bullet\bullet}$ is exceedingly favorable than the one between Mg_{Ti}'' and $\text{Nb}_{\text{Ti}}^{\bullet}$ ($\sim 3.95\text{\AA}$ apart), suggesting that there are uncoupled $\text{Nb}_{\text{Ti}}^{\bullet}$ defects that sit at the shallow donor level in the forbidden gap of the BST. These $\text{Nb}_{\text{Ti}}^{\bullet}$ defects likely act as fixed positive trapping centers³⁴ for electrons injected from the metal electrodes thus reducing the LC. Consequently, the BMN doped film requires larger bias voltage (>10 V, see Fig. 3(b)) to free trapped electrons so that substantial current is observed in the material.

3.3. Carrier transport mechanism in the films

The carrier transport in BST film has been frequently attributed to interface and bulk limited conduction mechanisms. The interface limited conduction mechanisms control the transport of carriers from electrode to the ferroelectric film through the potential barrier created at the interface. SE^{35–37} and Fowler–Nordheim tunneling^{35,37} are typical models that belong to the interface controlled transport mechanisms.

In the bulk limited mechanisms, the conduction of carriers is limited by the properties of the film (e.g., presence of shallow trap levels in forbidden gap of the material). Space charge limited conduction (SCLC)³⁷ and PF emission^{37–39} are some of the models that are used to describe the bulk limited conduction mechanisms.

Even though no single mechanism can fully describe the nature of carrier transport in BST, the strong temperature dependence (Fig. 3) of LC suggests that either the SE^{35,36} or the PF emission^{38,39} dominates the conduction mechanism in our BST films. To identify the possible transport mechanism in the BST films, the LC data were tested in light of the SE and PF models. The relation between current density J and applied electric field, E , for the SE^{35,36} and PF^{38,39} are given by

$$J = A^* T^2 \exp \left(-q \left(\varphi_b - \sqrt{qE/4\pi\epsilon_o\epsilon_r} \right) / kT \right) \quad (3)$$

and

$$J = q\mu N_C E \exp \left(-q \left(\varphi_t - \sqrt{qE/\pi\epsilon_o\epsilon_r} \right) / kT \right), \quad (4)$$

respectively, where A^* is the Richardson constant, q is electronic charge, T is the temperature, $q\varphi_b$ is the Schottky barrier height, μ is the electron mobility, N_C is the effective electron density of states in the conduction band, $q\varphi_t$ is the trap ionization energy, ϵ_o is the permittivity of free space, ϵ_r is the dynamic permittivity (high frequency permittivity) of the BST film. In each case, the applied electric field lowers the potential barrier (SE) or trapping potential (PF) for the electrons to escape. The two mechanisms are due to the columbic interaction between the escaping electron and a positive charge; but, they differ in that the positive charge is fixed for the PF trap ionization potential, while it is a mobile image charge for Schottky barrier.³⁷

Rearranging Eqs. (3) and (4), one can obtain linear relationships between $\ln(J/T^2)$ and $\sqrt{E}$ and $\ln(J/E)$ and $\sqrt{E}$ for the SE and PF models, respectively.^{35,37} If the carrier transport is dominated by the SE model, the $\ln(J/T^2)$ versus $\sqrt{E}$ graph will be linear where the slope results in a dynamic dielectric constant and the intercept can be used to estimate the potential barrier height. Likewise, if the conduction mechanism is controlled by the PF model, the $\ln(J/E)$ versus $\sqrt{E}$ graph will be linear and the slope is used to extract the dynamic dielectric constant while the trap ionization potential can be approximated from the intercept.

Figure 4 presents the graph of linear fitted $\ln(J/T^2)$ versus $\sqrt{E}$ for undoped BST film at variable temperature showing that the current data satisfy the SE model well; particularly at higher field region. However, for the SE to dominate the conduction mechanism in the film, the dynamic dielectric constant and potential barrier that are extracted from the slopes and intercepts of the linear fit must convey a physical meaning. The dynamic dielectric permittivity values calculated from the slopes of the linear fit to the SE and PF models at all the temperature ranges is shown in Table 1.

Fig. 4. $\ln(J/T^2)$ versus $\sqrt{E}$ for the undoped BST film linearly fitted (red lines) to estimate the ϵ_r and $q\varphi_b$ using the SE model.

The refractive index of BST, determined by optical method at a wavelength of 640 nm, is roughly 2.0 so that the high frequency dielectric permittivity value, $\epsilon_r = n^2$, is about 4.⁴⁰ The values of ϵ_r extracted from the SE plots for the undoped BST film are in the range of 5.76 to 1.49 (Table 1, column 2), decreasing with the increase of temperature from 300 to 450 K. These ϵ_r values agree well with the reported results ranging between 3.5 and 6.0.^{36,39–42} The well-fitted curve along with the rational ϵ_r values confirm that the SE is the dominant conduction mechanism in the undoped BST film. Conversely, the ϵ_r values extracted by fitting the current data for the doped film against the SE model (data not shown) were found to be unrealistically small (ranging from 1.50 to 0.47, see Table 1, column 3), suggesting that the conduction method in the BMN doped BST film is non-SE mechanism.

The current data for the BMN doped BST thin film were further tested against the PF model. Figure 5 shows the graph of $\ln(J/E)$ versus $\sqrt{E}$ for the BMN doped BST film. The high field region data fit well with PF model at all temperature ranges, leading to dynamic dielectric permittivity ranging from 8.85 to 3.85 (Table 1, column 5) that fall well within the typical range.^{24,27–30} The result suggests that, unlike the undoped BST film, the PF model is the dominant conduction mechanism in the doped BST thin film. A similar analysis on the undoped BST film (data not shown) indicates that the conduction mechanism in the film cannot be controlled by the PF conduction mechanism since the extracted ϵ_r parameters are very large (54.4 to 9.0, see Table 1, column 4).

The $q\varphi_b$ for the undoped BST and $q\varphi_t$ for the BMN doped BST films were estimated from the intercept values. When Eqs. (3) and (4) are linearized with respect to $\sqrt{E}$, the terms in the intercept takes the form $F(T) = \ln(A^*) - \frac{q\varphi_b}{kT}$ for the SE model, and $G(T) = \ln(q\mu N_C) - \frac{q\varphi_t}{kT}$ for the PF model, where $F(T)$ and $G(T)$ represent temperature-dependent intercept values. Since the current measurement in both films were performed at four different temperature values, four linear equations with two variables, (i.e., $\ln(A^*)$ and $q\varphi_b$) for the SE model, and $(\ln(q\mu N_C))$ and $q\varphi_t$ for the PF model) were obtained. These equations were solved using least squares

Table 1. ε_r extracted from the linear fit to the LC data to the SE and PF models.

Temperature (K)	SE: $\ln(J/T^2)$ versus $\sqrt{E}$		PF: $\ln(J/E)$ versus $\sqrt{E}$	
	ε_{r-} undoped BST (Fig. 4)	ε_{r-} -BMN doped BST (data not shown)	ε_{r-} undoped BST (data not shown)	ε_{r-} BMN doped BST (Fig. 5)
300	5.76	1.51	54.40	8.85
375	4.75	0.78	16.87	4.59
400	3.67	0.65	9.54	3.89
450	1.49	0.47	8.67	3.82

Fig. 5. (Color online) $\ln(J/E)$ versus $\sqrt{E}$ for the BMN doped BST film linearly fitted (red lines) to estimate the ε_r and $q\varphi_t$ using the PF model.

approximation method from which potential barrier height of 1.3 eV and trap ionization potential of 0.4 eV for the respective films were extracted. Interestingly, the numbers are found to be fairly comparable with the reported barrier height for the SE model,^{35,36,43} and trap ionization energy for PF model^{39,43} in BST and related perovskite thin films. The analysis in both films revealed that while the formation of Schottky potential barrier at the interface dominates the carrier transport in the undoped BST film, the BMN doped BST film is controlled by traps sitting in bulk of the film. The trap in the BMN doped film is expected to be due to the uncoupled $\text{Nb}_{\text{Ti}}^\bullet$ that sits at the shallow donor level in the forbidden gap of the BST. These $\text{Nb}_{\text{Ti}}^\bullet$ defects act as a fixed positive trapping center³⁴ for electrons; leading to the bulk dominated carrier transport in the BMN doped film.

3.4. FOM of the films

Analyzing the effect of BMN dopant on the tunability, dielectric loss, and FOM is critical to identify whether the doping through charge neutrality compensation will have influence on the BST film for practical application. Figure 6 shows the room temperature DC field (E) dependence of relative permittivity, ε_r , and $\tan \delta$ for both undoped and

Fig. 6. (Color online) The relative permittivity, ε_r , and $\tan \delta$ for the undoped (black) and BMN doped (red) BST thin films as a function of applied electric field, E .

BMN-doped BST films. The bell-shaped dependence of permittivity on bias field verifies that both films are in a paraelectric phase, suggesting that they do not exhibit a hysteresis behavior which is undesirable for their application in agile microwave devices.⁴⁴ The maximum dielectric constant (at zero bias) for the undoped and BMN doped films are 930 and 615, respectively. The decrease in dielectric constant for the doped film has been attributed to the reduced grain growth (see Fig. 1) observed in the doped BST film due to the grain pinning effects of both Mg and Nb ions.^{16,21,22}

The field-dependent tunability of ferroelectric varactors is defined as $\frac{\varepsilon(0) - \varepsilon(E)}{\varepsilon(0)} \times 100\%$, where $\varepsilon(0)$ and $\varepsilon(E)$ represent the dielectric constant at zero and applied electric field, respectively. Figure 7(a) shows the increase of tunability with the applied electric field for both films. The tunability of the BMN doped film is slightly lower than that of the undoped film in the entire field region. At the maximum applied bias field (640 kV/cm), 78% and 72% tunability values were measured for the undoped and BMN-doped BST films, respectively. This decrease in tunability for the BMN doped film is negligible compared with the effect that only Mg ion would have on tunability (reduces by up to $\sim 40\%$ with 5 mol % doping level).^{4,11} Moreover, the BMN doping has resulted in a remarkable decrease in the dielectric loss of the BST film

Fig. 7. (Color online) The tunability (a) and FOM (b) for undoped (black) and BMN doped (red) BST films as a function of applied bias field, E .

(see Fig. 6). The loss tangent of the BMN doped film is reduced by $\sim 38\%$ (loss tangent decreased from 0.048 to 0.03) compared with the undoped film.

It is known that the nonlinear behavior of BST's dielectric constant — making it essential for microwave application — with the applied electric field is due to the displacement of Ti ion within an oxygen octahedron (O_h).⁴⁵ Given the fixed space within the oxygen octahedron, the size or radius (R) of the ion that substitute Ti^{4+} has direct influence on altering the dielectric properties of BST. In this particular case, replacing Ti^{4+} ($R_{Ti} = 0.75 \text{ \AA}$) with Mg^{2+} ($R_{Mg} = 0.86 \text{ \AA} > R_{Ti}$) and Nb^{5+} ($R_{Nb} = 0.69 \text{ \AA} < R_{Ti}$) results in two opposing effects. The large Mg^{2+} occupies wider space and its rattling at the center of the oxygen octahedron is limited. On the other hand, the small Nb^{5+} resides in a lesser space and promotes ionic displacement.^{10,46} This contending effect between the two ions in the oxygen octahedron curtails the drop in tunability that would be caused if only an Mg dopant was used. Likewise, the decrease of dielectric loss can be attributed to the coupling of Mg charged defect with oxygen vacancy. When Oxygen vacancy couples with Mg defect in forming defect dipole, hopping of electrons generated from oxygen vacancy between different Ti ions^{5,32} is inhibited, thus lowering the dielectric loss.

From the device point of view for microwave application, the trade-off between tunability and dielectric loss is crucial. A FOM ($FOM = \frac{\epsilon(0) - \epsilon(E)}{\epsilon(0) \tan \delta} \times 100\%$) is a simple and handy parameter that reflects the trade-off between these two quantities for best device performance.² Figure 7(b) compares the FOM of the doped and undoped BST films as a function of applied field. Due to the slight decrease in tunability, but substantial drop in the dielectric loss, the FOM for the BMN doped BST film is remarkably higher than that of the undoped BST film. This suggests that the acceptor (Mg^{2+}) and donor (Nb^{5+}) co-doping through the complex BMN

oxide allows to obtain a good quality BST film that can be applied for agile microwave components than the undoped film.

4. Conclusions

In summary, taking full advantage of the large tunability of pure BST is challenging as it is accompanied by high dielectric loss and LC. By doping BST with BMN, we have shown a tread-off between dielectric loss and tunability. The doping of BST with BMN has remarkably reduced the dielectric loss with minor drop in tunability, leading to a higher FOM. The simultaneous substitution of Ti^{4+} with bigger size Mg^{2+} and smaller Nb^{5+} is responsible for upholding the tunability of the doped film close to that of the undoped film; while the coupling between Mg_{Ti}'' and $V_O^{\bullet\bullet}$ suppressed the dielectric loss by cutting electrons from hopping between Ti ions. The BMN doping has resulted in decreased LC attributed to the formation of defect dipoles between Mg_{Ti}'' , $V_O^{\bullet\bullet}$ and $Nb_{Ti}^{\bullet}$ charged defects that act as insulating layers, and uncoupled $Nb_{Ti}^{\bullet}$ trap centers. The surface morphology and chemical composition studies have shown that the BMN doping has resulted in smoother film surface with lower oxygen vacancy consistent within the reduced loss and LC of BST films. The dominant transport mechanism in the films was identified by analyzing the measured current data in light of the SE and PF models. While the carrier transport in the undoped BST film is observed to be interface limited (SE), that of the BMN doped film was bulk limited (PF). The change of the conduction mechanism from SE to PF is attributed to the presence of $Nb_{Ti}^{\bullet}$ sitting as a positive trap center at the shallow donor level of the forbidden gap of the BST film.

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