Dielectric dispersion of BiFeO$_3$ thin film over a broad frequency range (100 Hz–10 GHz)

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The dielectric properties of single-phase BiFeO$_3$ (BFO) thin films were investigated based on parallel-plate electrode (PPE) and coplanar interdigital electrode (CIE) configurations across a wide frequency range of 100 Hz–10 GHz. The dielectric dispersion in the PPE configuration, caused by the interfacial polarization in film/electrode interfaces, exhibited a strong dependence on frequency. In the CIE configuration, the low dielectric dispersion, high permittivity, and low dielectric loss indicated that interfacial polarization was substantially suppressed, revealing the dielectric properties of BFO film. Analysis of its electrical behavior demonstrated that Poole–Frenkel emission dominated the leakage current mechanism in the symmetric electrode structure. © 2009 American Institute of Physics. [DOI: 10.1063/1.3062857]

Multiferroic materials have attracted increasing interest due to their potential application in multifunctional devices.$^{1–3}$ BiFeO$_3$ (BFO) is one of the most extensively studied multiferroic materials since it exhibits large spontaneous polarization of $\sim 50 \ \mu$C/cm$^2$, high Curie temperature of $T_C \sim 1100$ K, and high Néel temperature of $T_N \sim 620$ K.$^{4,5}$ It is generally accepted that Schottky barriers, existing between a metal electrode and an insulating or semiconducting film, intensely affect the dielectric properties and ferroelectric measurement. Recently, Liu et al.$^5$ addressed the effect of interfacial polarization on the dielectric properties in In/BFO/La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO)/SrTiO$_3$ (STO) with parallel-plate electrode (PPE) structure. The capacitance and tunability exhibited a sharp decrease above the frequency of 1 MHz, which stemmed from Schottky contacts between BFO film and electrodes due to the fact that the work functions of In ($\sim 4.3$ eV) and LSMO ($\sim 4.96$ eV) were much higher than the electron affinity of BFO ($\sim 3.03$ eV).$^6$ In Pt/BFO/Pt symmetric electrode structure, the dielectric constant of BFO decreased about 30% from 1 KHz to 1 MHz, showing $e_r \sim 130$ at $f=1$ MHz.$^7$ Using the PPE configuration, the dielectric constant for BFO materials was reported to be $\sim 110$–170 in granular films$^8$ and $\sim 50$–80 in polycrystalline bulk materials.$^9,10$ In order to investigate the dielectric properties of BFO film, both PPE and coplanar interdigital electrode (CIE) configurations were fabricated and the dielectric properties of BFO film were systematically studied over a wide frequency range from 100 Hz to 10 GHz.

The BFO film was grown on single crystalline LaAlO$_3$ (00l) (LAO) substrate by pulsed laser deposition using a KrF excimer laser ($\lambda=248$ nm). In this case, LaAlO$_3$ ($e_r$$_{\text{LAO}} \sim 24$) was selected as the substrate because a SrTiO$_3$ substrate with large permittivity of $e_r$$_{\text{STO}} \sim 320$ will affect the dielectric properties measurement when using CIE configuration. Bi$_{1.1}$FeO$_3$ ceramic was used as the target and the excess bismuth was added to compensate for the Bi volatilization during deposition. A substrate temperature of 550 °C and an oxygen pressure of 50 mTorr were used for the deposition of BFO film. Then, the BFO film was annealed in situ in oxygen at 650 °C for 60 min to facilitate crystallization. For BFO film depositing on Pt(200 nm)/TiO$_2$/SiO$_2$/Si substrate, the detailed deposition conditions were referred to that by Yun et al.$^1$ To fabricate the interdigital electrodes, 10 nm chromium and 30 nm Au were first deposited by rf magnetron sputtering as seed layers, respectively. Then a layer of $\sim 2$ μm Au as the top electrode was electroplated on seed layer in order to reduce the microwave losses. Finally, the CIE was prepared by photolithographic techniques using hard mask. The dielectric properties were measured by an HP4192A LF impedance analyzer at low frequency and by a PNA Series Network Analyzer (Agilent N5230A) at microwave frequency from 0.5 to 10 GHz.

Figure 1 shows the x-ray diffraction (XRD) patterns of BFO film depositing on LAO and Pt/TiO$_2$/SiO$_2$/Si substrate, respectively. Besides the peaks of (104) and (110) for BFO, the pattern mainly shows strong peaks corresponding to (00l) reflections of BFO and those from the LAO substrate, indicating that BFO is well oriented on the LAO substrate without undergoing an impurity phase. The XRD result

FIG. 1. (Color online) XRD patterns of BFO thin film depositing on LAO and Pt substrate. Inset shows surface scanning electron micrographs of BFO film on LAO.
of depositing on Pt also indicates that polycrystalline film is a single phase.\(^7\) The field emission scanning electron microscope (SEM, JEOL JSM-6700F) image is shown in the inset of Fig. 1. The surface image demonstrates a dense surface morphology with a grain size of about 100 nm. The thickness of the BFO film is determined to be of \(\sim 360\) nm for depositing on Pt and \(\sim 310\) nm for depositing on LAO substrate from cross-sectional SEM image.

Figure 2 gives the dielectric properties of BFO film as a function of measuring frequency from 100 Hz to 10 MHz. In Pt/BFO/Pt structure, the permittivity \(\varepsilon_{\text{PPE}}\) is obtained according to measured capacitance \(C, \varepsilon_{\text{PPE}}=Cd/\varepsilon_0A\), where \(d\) is the film thickness and \(A\) is the electrode area. The \(\varepsilon_{\text{PPE}}\) changes from 170 at 100 Hz to 106 at 10 MHz, decreasing about 37\% with the increase in frequency, as seen in Fig. 2(a). Generally, the dielectric dispersion results from the interfacial polarization in PPE configuration, namely, the Maxwell–Wagner relaxation caused by space charge polarization in film/electrodes interfaces.\(^{10}\) The dielectric loss factor tan \(\delta\) also decreases with frequency and is lower than 0.08 within the investigated frequency range. The tunability, defined as \(\tau=|\text{C}(0)−\text{C}(V)|/\text{C}(0)\times 100\%\), reaches \(\tau=9.25\%\) under 5 V dc bias at \(f=1\) kHz and displays a certain butterfly sharp of C-V loops, as shown in the inset of Fig. 2(a). The tunable effect in present Pt/BFO/Pt structure is consistent with \(\tau \sim 28\%\) under 15 V by Yun et al.\(^7\)

Figure 2(b) displays the low frequency dielectric properties based on CIE configuration. The permittivity \(\varepsilon_{\text{CIE}}\) based on the CIEs can be calculated using the following expression:\(^{13,14}\)

\[
\varepsilon_{\text{CIE}} = \varepsilon_r + \frac{C-K(1+\varepsilon_s)}{K[1-\exp(-4.6h/(g+w))]},
\]

where \(\varepsilon_r=24\) is the dielectric constant of LAO substrate, \(h=310\) nm is the film thickness, and \(g=11.2\) \(\mu\)m and \(w=8.8\) \(\mu\)m are the width of gap and finger measured from the microscope, as seen in the inset of Fig. 2(b). \(K\) is the constant in units of picofarads, is related to the \(g\) and \(w\), and can be expressed by

\[
K = 6.5 \left(\frac{g}{g+w}\right)^2 + 1.08 \frac{g}{g+w} + 2.37.
\]

\(C\) is the capacitance per unit finger length per electrode section of width and is given by \(C = C_m/(LN)\), where \(C_m\) is the measured capacitance, \(L=180\) \(\mu\)m is the overlapping length for interdigital fingers, and \(N=8\) is the number of gaps for interdigital capacitor. According to measured capacitance, the permittivity \(\varepsilon_{\text{CIE}}\) at low frequency also exhibits frequency-dependent characteristics and changes from \(-331\) at 100 Hz to \(-297\) at 10 MHz, showing a 10\% decrease. Notably, the dielectric loss tan \(\delta\) in CIE is about 0.04 in measured frequency range, also lower than tan \(\delta\) in PPE structure. Compared to 37\% decrease in \(\varepsilon_{\text{PPE}}\), it is suggested that the large dielectric dispersion stemming from the interfacial polarization plays an important role in PPE configuration rather than that in CIE structure. The low dielectric dispersion using CIE configuration can also be observed in \(\text{Ba}_{0.75}\text{Sr}_{0.25}\text{TiO}_3\) film and \(\text{Na}_0.5\text{K}_0.5\text{NdO}_3\) film at low frequency.\(^{15,16}\) Moreover, the obtained permittivity \(\varepsilon_{\text{PPE}}\) is much lower than permittivity \(\varepsilon_{\text{CIE}}\). It is considered that the interfacial polarization in PPE configuration can be equivalent to be a capacitor in series with the film capacitor, which results in the lower apparent capacitance.\(^17\) Therefore, the gentle dielectric dispersion behavior and low loss tan \(\delta\) strongly indicate that the interfacial polarization effect is well suppressed in CIE configuration.

Figure 3 displays the capacitance \(C'\) using CIE as a function of measuring frequency from 0.5 to 10 GHz. The capacitance is calculated based on measured S-parameter data \([S_{11}=(Z-Z_0)/(Z+Z_0)]\), where \(Z_0=50\ \Omega\). One can then obtain the real part \(C'\) and imaginary part \(C''\) of the capacitance.

FIG. 2. (Color online) (a) Dependence of the permittivity \(\varepsilon_{\text{PPE}}\) and loss tan \(\delta\) on the frequency in PPE configuration. Inset of (a) shows the C-V curves measured at a frequency of 1 kHz. (b) The permittivity \(\varepsilon_{\text{CIE}}\) and loss tan \(\delta\) as a function of frequency in CIE configuration. Inset of (b) displays the image and schematic diagram of the CIE.
tance and tan $\delta = C''/C'$ according to the load impedance $Z=R+1/j\omega(C'+jC)$.

It is found that obtained capacitance $C'$ is about 0.30 pF and depicts good frequency independent characteristics. From Eq. (1), the permittivity of BFO film is $\varepsilon_{\text{BFO}} = 241$ and loss tan $\delta = 0.037$ at frequency of 4 GHz. Under the applied voltage of dc 40 V, the capacitance decreases slightly and exhibits the tunability $\tau = 1.26\%$ at 4 GHz, as seen in the inset of Fig. 3. With the increase in frequency, the tunability changes from $\tau = 1.03\%$ at 6 GHz to 0.85% at 10 GHz. In view of previous reports, the large tunability of BFO was found in PPE structure, such as $\tau \sim 45\%$ in In/BFO/LSMO at 10 KHz and $\tau \sim 28\%$ in Pt/BFO/Pt at 1 MHz.5,7 Simultaneously, this remarkable tunability exhibited sensitive frequency-dependent behavior and dropped quickly with the increase in frequency. Based on the analysis of complex impedance spectra, Liu et al.4 revealed that a large tunability at low frequency was dominated by the interfacial polarization effect, i.e., approximate 60% tunable effect results from the contribution of electrode/film contacts. In the present work, the good frequency independence characteristics of the permittivity and tunability in microwave frequency region also substantially supported the observation that the interfacial polarization was well suppressed in CIE configuration.

Typical leakage data ($J$-$V$) as a function of applied positive and negative biases in Pt/BFO/Pt structure are shown in Fig. 4(a). Here, we also discuss the possible leakage current limiting mechanisms for BFO film based on the existing models,19,20 such as interface-limited Schottky emission $J = A T^2 \exp\left[-\Phi/k_B T - e\sqrt{V/4\pi \varepsilon_0 \varepsilon_{\text{opt}} d/k_B T}\right]$, bulk-limited space-charge-limited conduction (SCLC) $J = 9\mu e_0 e_\varepsilon V^2/8d^2$, and Poole–Frenkel emission $\sigma_{\text{PF}} = B \exp\left[-\Phi/k_B T - e\sqrt{V/4\pi \varepsilon_0 \varepsilon_{\text{opt}} d/k_B T}\right]$, where $\Lambda$ and $B$ are constants and $\Phi$ and $\Phi'$ are the height of the Schottky barrier and the trap ionization energy, respectively. $\varepsilon_{\text{opt}}$ is the optical dielectric constant, $\mu$ is the charge carrier mobility, and $d$ is the film thickness. By plotting experimental data in various manners as a function of voltage, one can quickly obtain insight into the nature of the leakage mechanism. The SCLC is not the dominant leakage mechanism because an exponential fitting describes better than a linear fitting in Fig. 4(b). In the case of Schottky emission and Poole–Frenkel emission, as shown in Figs. 4(c) and 4(d), semilog plots of $J/T^2$ versus $V^{0.5}$ and $\sigma$ versus $V^{0.5}$ show regions with straight fits to the data. We extracted the optical refractive index $n = (\varepsilon_{\text{opt}})^{1/2}$ from the linear part of the plots above an applied field of ~90 kV/cm and obtained the optical dielectric constants $\varepsilon_{\text{opt}}$ of 0.816 for the Schottky barrier and 9.351 for the Poole–Frenkel emission. It is noted that the optical refractive index $n$ has been reported to be of 2.5–3.1 for BFO.19–21 Therefore, the optical dielectric constant $\varepsilon_{\text{opt}}$ extracted from Poole–Frenkel emission is close to the expected relative permittivity of 6.25–9.61. This suggests an onset of the influence of Poole–Frenkel emission effect in the region of applied field.

The dielectric properties of BFO film were investigated based on PPE and CIE configurations in a frequency range from 100 Hz to 10 GHz. In contrast to the dielectric properties in the PPE configuration, high permittivity $\varepsilon_{\text{CIE}}$, low loss tan $\delta$, and gentle dielectric dispersion were observed in CIE configuration, which indicated that interfacial polarization caused by space charges in the film/electrode interface was effectively suppressed by the use of coplanar electrodes. According to an analysis of their electrical behavior, Poole–Frenkel emission dominates the leakage current mechanism in the symmetric electrode structure.