Effects of interfacial polarization on the dielectric properties of $BiFeO_3$ thin film capacitors

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Epitaxial $BiFeO_3/La_{0.7}Sr_{0.3}MnO_3$ (BFO/LSMO) heterostructures were grown on $SrTiO_3$ (001) substrates. Dielectric properties of the BFO thin films were investigated in an In/BFO/LSMO capacitor configuration. The capacitance of the capacitor shows strong dependences on measuring frequency and bias voltage especially in low frequency region ($\leq$1 MHz). By means of complex impedance analysis, it is found that the interfacial polarization caused by space charges in the film/electrode interfaces plays an important role in the dielectric behavior of the capacitor. Our results indicate that the influences of film/electrode interfaces might not be neglected on the dielectric properties of the BFO thin film capacitors. [DOI: 10.1063/1.2900989]

Multiferroic materials which combine ferromagnetism and ferroelectricity have attracted much attention due to their potential applications in multifunctional devices. Among them, $BiFeO_3$ (BFO) has been widely studied since it exhibits a large spontaneous polarization (50–60 $\mu C/cm^2$),[1] a high Curie temperature ($\sim$1123 K),[2] and a high Néel temperature ($\sim$625 K).[3] Generally, bottom and top metal electrodes, which make Schottky contacts with the BFO thin film,[4] are fabricated to form a capacitor configuration for dielectric and ferroelectric measurements. The performance of ferroelectric films is often affected by the electrode interfaces and the interfaces may play an important role in the properties of ferroelectric films.[5–7] BFO thin films usually suffer large leakage current due to the oxygen vacancies and Fe^{2+} in the samples[8,9] so interface effects could be more notable in the semiconductorlike BFO thin film capacitors. Lee *el al*. have found that the film/electrode interfaces greatly affect the leakage current of BFO thin films.[10] So far, however, few reports are available about the interface effects on the dielectric behavior of BFO thin film capacitors. It is well known that complex impedance analysis is a powerful tool to separate dielectric relaxations from the bulk, electrodes, and grain boundaries for dielectric materials. In this letter, BFO thin film capacitors were studied by impedance analysis. The results show that the dielectric properties of the BFO capacitor at frequencies lower than 1 MHz are greatly affected by the interfacial polarization caused by the space charges in the film/electrode interfaces.

$La_{0.7}Sr_{0.3}MnO_3$ (LSMO) bottom layer and BFO thin film were epitaxially grown on $SrTiO_3$ (STO) (001) substrates by laser molecular-beam epitaxy.[11] For BFO thin films, a $Bi_{1.15}FeO_3$ ceramic was used as the target and the excess bismuth is to compensate for the Bi volatilization during deposition. First, a 300-nm-thick LSMO layer was deposited on STO substrate at a temperature of 650 °C; then, a 350-nm-thick BFO thin film was grown on LSMO/STO at 500 °C. Oxygen pressure was kept at 0.2 Pa during the deposition process. After that, the samples were *in situ* annealed for 30 min under the deposition conditions and then cooled to room temperature. Indium (In) slat with 1 mm^2 was pressed on the surface of the BFO as the top electrode and LSMO layer acted as the bottom electrode. The crystal structure of the BFO/LSMO heterostructure was characterized by x-ray diffraction (XRD). The dielectric properties of the capacitor were measured at room temperature by an Agilent 4294 impedance analyzer with frequency ranging from 100 Hz to 100 MHz.

Figure 1 shows a typical θ-2θ XRD pattern of the BFO/LSMO heterostructure on STO substrate. The pattern only shows strong peaks corresponding to (00l) reflections of BFO and those from the STO substrate and LSMO layer, indicating that both BFO and LSMO layers were epitaxially grown on STO substrate without impurity phases. The out-of-plane lattice constant of the BFO calculated from the (002) peak is $\sim$3.956 Å (pseudocubic unit), being close to its bulk value (3.96 Å).

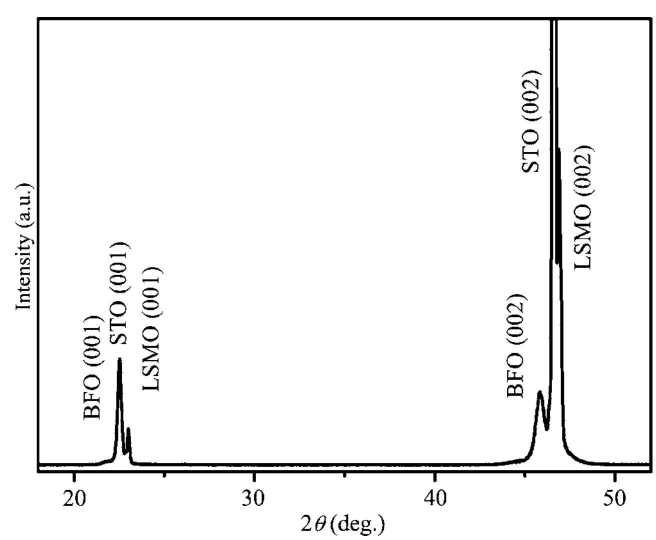

FIG. 1. XRD profile of the BFO/LSMO heterostructure on STO (001) substrate.

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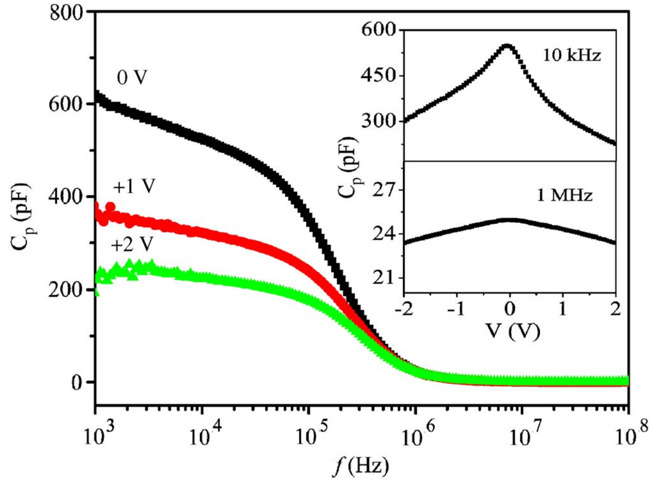

FIG. 2. (Color online) The frequency dependence of the capacitance of the In/BFO/LSMO capacitor under forward biases. The inset shows the C_p-V characteristics of the In/BFO/LSMO capacitor at 10 kHz and 1 MHz. The ac oscillation voltage was 50 mV.

Figure 2 shows the capacitance-frequency (C_p-f) curves of the capacitor measured with different forward biases at room temperature. In the present study, forward bias represents that the positive voltage is applied to the LSMO bottom electrode. The capacitance dramatically decreases with increasing frequency especially in the frequency range of 10 kHz–1 MHz. Moreover, the capacitance significantly decreases with increasing bias voltage in the low frequency range. The inset of Fig. 2 shows the room temperature capacitance-voltage (C_p-V) curves measured at 10 kHz and 1 MHz. The capacitance of the BFO thin film capacitor exhibits a high tunability [defined as $C_p(0)/C_p(V)-1$] at 10 kHz and the tunability at 2 V rapidly decreases from 80% at 10 kHz to less than 10% at 1 MHz.

To investigate the origin of the observed dielectric behavior, the complex impedance analysis was performed on the BFO capacitor. Figure 3(a) shows the complex impedance plot (Z' versus Z'', where Z' and Z'' are the real and imaginary parts of the total impedance, respectively) for the BFO capacitor under forward biases. Similar to that for $LaAlO_3$ capacitor,[12] almost two semicircles can be observed at a preliminary glance. With the increase of applied bias voltage, the arc in the lower frequency region (LF region) is greatly depressed, whereas the arc in the higher frequency region (HF region) is almost unchanged. Similar behavior has also been observed under reverse biases. To clarify that the semicircle arc in the low frequency range [shown in Fig. 3(a)] contains one or two overlapped arcs, a corresponding plot of Z' versus Z''/f of the impedance spectrum under zero bias is shown in Fig. 3(b) and three well defined regions with different slopes are observed. The alternative Z' versus Z''/f representation, proposed by Abrantes *et al.*,[13] can distinguish the contributions from different relaxations with relatively small differences in time constants. Accordingly, the three regions in the frequency range of $f<5.8\times10^3$ Hz, 5.8×10^3 Hz$<f<7\times10^6$ Hz, and $f>7\times10^6$ Hz may originate from three different dielectric responses, respectively. In principal, for bulk ceramic material, the three observed responses from low to high frequencies can be attributed to the contributions from electrodes, grain boundaries, and bulk, respectively. In our case, similar to previous report,[14] for the epitaxial BFO thin film, there is no grain boundary and only bulk and interfaces (film/electrode) could contribute to the dielectric relaxations. Therefore, the HF region ($f>7\times10^6$ Hz) without obvious voltage dependence corresponds to the dielectric response from bulk and the two LF regions correspond to the dielectric responses from the top and bottom interfaces.[14] According to our previous report, the dielectric response from the interface between ferroelectric and LSMO layer is dominant in the frequency region between kilohertz and megahertz.[15] So, it might be speculated that the dielectric response of the BFO capacitor in the region of $f<5.8\times10^3$ Hz corresponds to the In/BFO top interface and that in the region of 5.8×10^3 Hz$<f<7\times10^6$ Hz corresponds to the BFO/LSMO bottom interface.

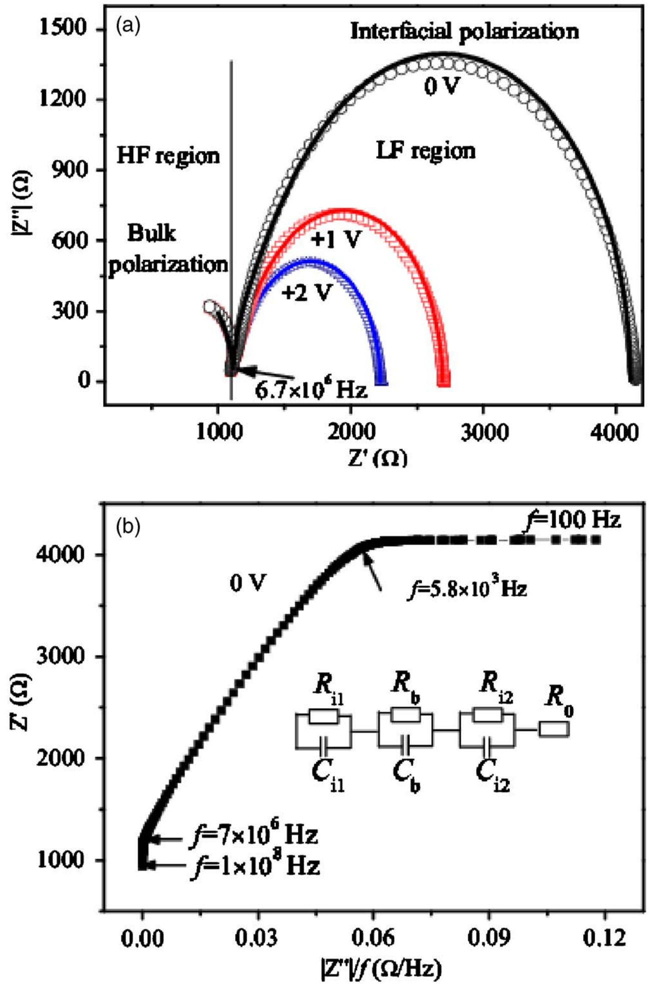

FIG. 3. (Color online) (a) Complex impedance spectra of the In/BFO/LSMO capacitor under different dc biases, the vertical line shows the demarking frequency where the polarization changed from interfacial polarization to bulk polarization. The solid lines through the date points are the fitting results obtained by a series of three parallel *RC* circuits. (b) Representation of Z' vs $|Z''|/f$ for the complex impedance spectrum under zero bias; the inset displays the equivalent fitting circuit.

The complex impedance plot can be well fitted by using a series of three parallel *RC* circuits [shown in the inset of Fig. 3(b)]. The solid lines in Fig. 3(a) represent the fitting results, which perfectly fit the data points. Table I shows the fitting parameters, where C_b and R_b, R_{i1} and C_{i1}, and R_{i2} and C_{i2} describe the capacitances and resistances of the bulk and the interfaces of In/BFO and BFO/LSMO, respectively. According to the fitting result, the relaxation time, defined as $\tau=RC$, of 5.18×10^{-10} s for bulk is far less than that of 4.1×10^{-7} and 2.98×10^{-6} s for the top and bottom interfaces,

TABLE I. Fitting parameters of Fig. 3(a) using the equivalent circuit shown in the inset of Fig. 3(b), where R_{i1}, C_{i1} describe the In/BFO interface, R_{i2}, C_{i2} describe the BFO/LSMO interface, and C_b, R_b describe the bulk.

Bias voltage	Interface			Bulk		
V (V)	R_{i1} (Ω)	C_{i1} (nF)	R_{i2} (Ω)	C_{i2} (nF)	R_b (Ω)	C_b (pF)
0	250	1.64	2743	1.086	826	0.628
+1	160	1.43	1420	1.009	867	0.573
+2	131	1.39	983	1.002	883	0.537

respectively. For a circuit composed of a series of two parallel RC elements (R_1, C_1, and R_2, C_2), two arcs will be well separated in the Z' versus Z'' plot when the values of R_1C_1 and R_2C_2 are quite different.[16] In Fig. 3(a), the overlapping arcs in the LF region can be related to the close relaxation times for the top and bottom interfaces. Generally, the film/electrode interfaces can cause Maxwell–Wagner-type relaxations by the space charge polarization in depletion layers.[17] In our case, BFO forms Schottky contacts with In and LSMO because the work functions of In (~4.3 eV) and LSMO (4.96 eV) (Ref. 18) are larger than the electron affinity of n-type BFO (3.3 eV).[4] We may term the Maxwell–Wagner relaxation from the two film/electrode interfaces as interfacial polarization. The capacitance C_i related to the interfacial polarization is much larger than the C_b of bulk. Since the capacitance C_i results from the depletion layer of the electrode/film interfaces, the suppression of applied voltage V on C_i can be well understood by the following relation:

$$C = \sqrt{\frac{e\varepsilon' N_d}{2(V_d + V)}},$$

where N_d is the donor concentration and V_d is the diffusion potential.[19] As discussed in Fig. 3, the interfacial polarization is significant in the LF region since the dielectric responses from the two interfaces are dominant in the frequency region of $f < 7 \times 10^6$ Hz. Thus, the capacitance of the capacitor obviously decreases with the increase of applied voltage at low frequencies, as shown in the inset of Fig. 2. It is noticed that the capacitance from depletion layer in diodes rapidly decreases with the increase of frequency at low frequencies[20,21] and the Maxwell-Wagner-type interfacial polarization can cause an intense drop of the dielectric constant in the frequency range of 100 Hz–100 kHz in $(Ba,Sr)TiO_3$ capacitors.[22] The sharp decrease in the capacitance of the In/BFO/LSMO capacitance with increasing frequency at low frequencies can also be attributed to the interfacial polarization effect. Therefore, it can be concluded that the interfacial polarization leads to the strong dependences of the capacitance of BFO thin film capacitors on frequency and bias voltage at low frequencies.

In summary, the dielectric properties of In/BFO/LSMO thin film capacitors were investigated. The capacitance obviously decreases with increasing bias voltage and frequency at low frequencies (≤1 MHz). Complex impedance analysis shows that the dielectric behavior of the BFO thin film capacitor is greatly affected by the interfacial polarization, resulting in the strong dependences of capacitance on frequency and bias voltage in low frequency region. The results suggest that further studies and attentions should be given to choose appropriate electrode contact for BFO thin films to alleviate the interface effects.

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