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. © 2008 American Institute of Physics.

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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$^2$), a high Curie temperature ($\sim$1123 K), and a high Néel temperature ($\sim$625 K). Generally, bottom and top metal electrodes, which make Schottky contacts with the BFO thin film, are fabricated to form a capacitor configuration for dielectric and ferroelectric measurements. The performance of ferroelectric films is often affected by the electrode interfaces and the interfaces may play an important role in the properties of ferroelectric films. BFO thin films usually suffer large leakage current due to the oxygen vacancies and Fe$^{2+}$ in the samples, so interface effects could be more notable in the semiconductorlike BFO thin film capacitors. Lee et al. have found that the film/electrode interfaces greatly affect the leakage current of BFO thin films. 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.

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FIG. 1. XRD profile of the BFO/LSMO heterostructure on STO substrate.
The inset of Fig. 2 shows the room temperature increases with increasing bias voltage in the low frequency 10 kHz – 1 MHz. Moreover, the capacitance significantly decreases with increasing frequency especially in the frequency range of 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 \((Z' \text{ versus } Z'')\), 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, 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 semicircular arc in the low frequency range [shown in Fig. 3(a)] contains one or two overlapped arcs, a corresponding plot of \( Z' \text{ versus } Z''/f \) 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 \( Z' \text{ versus } Z''/f \) representation, proposed by Abrantes et al., can distinguish the contributions from different relaxations with relatively small differences in time constants. According to previous reports, the dielectric response of the BFO capacitor in the region of \( f > 10^6 \) 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. 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. So, it might be speculated that the dielectric response of the BFO capacitor in the region of \( f < 5.8 \times 10^5 \) Hz corresponds to the In/BFO top interface and that in the region of \( 5.8 \times 10^5 \text{ Hz} < f < 7 \times 10^6 \) Hz corresponds to the BFO/LSMO bottom interface.

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 \( C_p \) and \( R_i \) and \( C_{i1} \) and \( R_{i2} \) and \( C_{i2} \) describe the capacitances and resistances of the bulk and interfaces (film/electrode) could contribute to the dielectric relaxations. Therefore, the HF region \(( f > 7 \times 10^6 \) 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.
respective. For a circuit composed of a series of two parallel RC elements \((R_1, C_1, R_2, C_2)\), two arcs will be well separated in the \(Z'\) versus \(Z''\) plot when the values of \(R_1 C_1\) and \(R_2 C_2\) 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).\(^{3}\) 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:

\[
C = \sqrt{\frac{\varepsilon \varepsilon_0 N_D}{2(V_d + V)}},
\]

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 (\(\leq 1\) 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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TABLE I. Fitting parameters of Fig. 3(a) using the equivalent circuit shown in the inset of Fig. 3(b), where \(R_1, C_1\) describe the In/BFO interface, \(R_2, C_2\) describe the BFO/LSMO interface, and \(C_p, R_p\) describe the bulk.

<table>
<thead>
<tr>
<th>Bias voltage (V) ((\text{V}))</th>
<th>Interface ((\Omega, \text{nF}))</th>
<th>Bulk ((\Omega, \text{pF}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>250, 1.64</td>
<td>1.086, 26, 0.628</td>
</tr>
<tr>
<td>+1</td>
<td>160, 1.43</td>
<td>1.009, 867, 0.573</td>
</tr>
<tr>
<td>+2</td>
<td>131, 1.39</td>
<td>1.002, 883, 0.537</td>
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