Enhanced tunability due to interfacial polarization in $La_{0.7}Sr_{0.3}MnO_3/BaTiO_3$ multilayers

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$BaTiO_3$ single layer and $La_{0.7}Sr_{0.3}MnO_3/BaTiO_3$ multilayer films were fabricated by laser molecular-beam epitaxy. The voltage tunability of these films was investigated systematically in the frequency ranging from 10 kHz to 1 MHz. The results suggest that the sizable tunability arises from the interfacial polarization which can be strongly suppressed by applied dc biases. In multilayer films, remarkable enhancement in voltage tunability was observed, because the interfacial polarization was greatly enhanced by an interfacial polarization associated possibly with the Maxwell-Wagner relaxation. The authors' results indicate that the voltage tunability in low frequency ($\leqslant$1 MHz) has a dominating contribution from the interfacial polarization. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2737368]

The nonlinear dielectric property of ferroelectric thin films, which shows a large dispersion at different ac amplitudes and dc biases, makes them very attractive for electrically tunable microwave devices.[1,2] To improve dielectric tunability and to lower dielectric loss, the crucial properties necessary for application of the tunable devices, lots of effort has been made during the last decade. On the one hand, different techniques such as sol gel,[3] rf sputtering,[4] and pulsed laser deposition[5] have been employed toward fabricating the optimum ferroelectric thin films. On the other hand, various effects such as doping, composition, strain, graded thin films, superlattices, etc.[6–10] on the dielectric property have been investigated with the aim to maximize the tunability. Recently, Kim *et al.*[10] reported a giant tunability as high as 94% in $BaTiO_3/SrTiO_3$ superlattice with the periodicity of two unit cells. The origin of the unexpected large tunability was ascribed to the stress-induced lattice distortion.[10,11] More recently, a numerical analysis,[12] however, indicated that a stress-free $BaTiO_3/SrTiO_3$ bilayer can show tunability greater than 90% due to electrostatic and electromechanical coupling between layers.

It is worth pointing out that the above-mentioned giant tunability was measured at a frequency of 1 MHz. While in the frequency range below and around megahertz, the interfacial polarization in the superlattices can drastically enhance the dielectric constant.[13,14] The improved property might, more or less, result from this extrinsic contribution. Besides, in this frequency range, the extrinsic polarizations arising from electrodes, grain boundaries, and *p-n* junctions also have significant contribution to the dielectric property and inevitably affect the dielectric tunability. In this letter, we show that the voltage tunability in the low-frequency range ($\leqslant$1 MHz) is dominated by the interfacial polarization. In multilayer films the interfacial polarization can be greatly enhanced, thereby improving the dielectric tunability.

The $BaTiO_3$ (BTO) thin film and multilayers of $La_{0.7}Sr_{0.3}MnO_3$ (LSMO)/BTO were epitaxially grown on $SrTiO_3$ (001) (STO) substrates by a computer-controlled laser molecular-beam epitaxy technique.[15] First, a 100-nm thick LSMO was deposited on the STO substrates as bottom electrode. Then, three samples denoted as F1, F2, and F15 were fabricated. F1 is one 300-nm-thick BTO thin film on the LSMO coated substrate, F2 is two 100-nm-thick BTO and one 100-nm-thick LSMO stacked alternately on the LSMO coated substrate, and F15 is eight 20-nm-thick BTO and seven 20-nm-thick LSMO stacked alternately on the LSMO coated substrate. The three samples were fabricated at the same growth condition and the total thickness of the films was controlled at about 300 nm. Details about the deposition conditions can be found elsewhere.[16] Dielectric measurements were carried out at room temperature using an Agilent 4294A precision impedance analyzer in a frequency range varying from 100 Hz to 110 MHz with sputtered Au as top electrodes. The ac measuring signal was 50 mV rms.

Figure 1 shows the electric field dependence of the normalized capacitance, $Cp(E)/Cp(E=0)$, for films of F1, F2, and F15 with different measuring frequencies. It is seen that the normalized capacitance exhibits a rapid drop in the low electric field range followed by a slow decrease at high fields. The rapid drop is more pronounced at 10 kHz in all films. But it gradually disappears in F1 and F2 with increasing measuring frequencies, as a result, only the slow de-

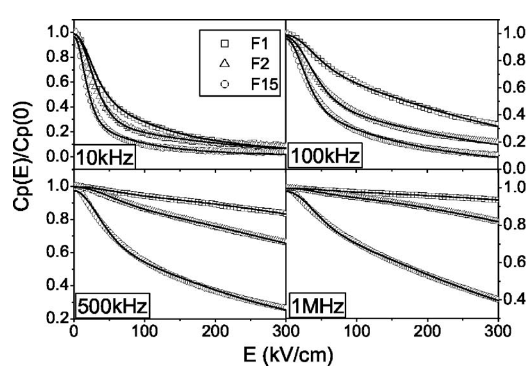

FIG. 1. Electric field dependence of the normalized capacitance for F1, F2, and F15 measured at different frequencies shown in the figure. The solid curves through the data points are the least-squares fitting results based on Eqs. (1) and (2).

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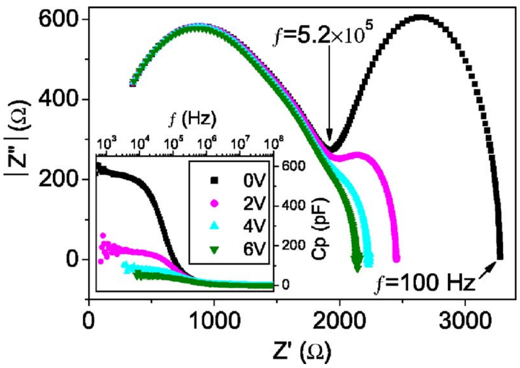

FIG. 2. (Color online) Complex impedance spectra of F1 under different dc biases. The inset shows the frequency dependence of the capacitance for F1 under these biases.

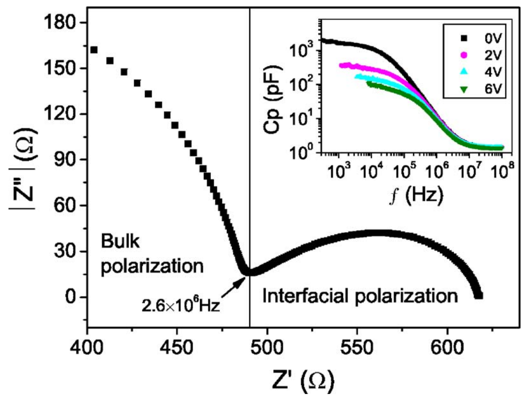

FIG. 3. (Color online) Complex impedance plot of F2. The vertical line indicates the demarking frequency where the polarization changes from interfacial type to bulk type. The inset shows the frequency dependence of the capacitance for F2 under different dc biases.

crease can be observed in F1 and F2 when the measuring frequency higher than 500 kHz. Whereas in F15 even at the highest measuring frequency (1 MHz), the rapid drop is still remarkable. This means that, by comparison with those of F1 and F2, the voltage tunability $[=1-Cp(E)/Cp(E=0)]$ of the multilayer film (F15) is greatly enhanced.

To clarify whether the enhancement in voltage tunability is related to the extrinsic polarizations, we performed impedance analysis, which is a well known technique to separate extrinsic polarization from bulk polarization.[17] Figure 2 displays the complex impedance plot (Z' vs Z'') for F1 under various dc biases. Two semicircular arcs were observed at a preliminary glance. However, a careful inspection reveals that the enhanced arc in the low-frequency range might contain two overlapping arcs. This is supported by an alternative presentation of Z' vs Z''/f (not shown) proposed by Abrantes *et al.*,[18] where three well defined regions in the frequency range of $f<2570$ Hz, $257<f<5.2\times10^5$ Hz, and $f>5.2\times10^5$ Hz are clearly seen. According to Ref. 18, these sequential regions from low to high frequencies correspond, respectively, to the dielectric response from electrodes, interfaces (grain boundaries), and bulk. The electrode response in the three investigated films was found to dominate in almost the identical frequency range, i.e., below ~2.5 kHz. The dielectric responses associated with the interface and electrode are the well known Maxwell-Wagner relaxation caused by space charge polarization at the interface between the two layers with different dielectric constants and conductivities, and will be generally termed as interfacial polarization in the present work. The interfacial polarization separates well from its bulk counterpart with the demarking frequency (f_d) at $\sim5.2\times10^5$ Hz. It can also be clearly seen that the applied dc biases strongly suppress the interfacial polarization, whereas the bulk polarization is almost independent of the biases. This is further confirmed by the result of the frequency dependence of the capacitance under different biases shown in the inset of the figure. The capacitance decreases rapidly with increasing frequencies convinces the interfacial nature of the dielectric behavior in the low-frequency region. It therefore follows that the efficacy of dc bias in suppression the interfacial polarization leads to the rapid drop in normalized capacitance at low frequencies (Fig. 1). When the measuring frequency higher than f_d, the bulk polarization dominates thereby causing the slim variation with increasing biases in normalized capacitance at high frequencies, as seen in Fig. 1.

Figures 3 and 4 show the complex impedance plots of F2 and F15, respectively. In comparison with the results of F1, remarkable changes can be seen: (1) Both the real (Z') and imaginary (Z'') parts of the complex impedance decrease as the number of LSMO layer increases. This might be ascribed to a percolativelike behavior that the increase of the conductive component (LSMO) largely enhances the conductivity. (2) f_d was found to be evidently enlarged with increasing LSMO and BTO layers. For example, f_d in F2 is ~2.6 MHz, which is one order of magnitude higher than that of F1; and f_d in F15 is 5.8 MHz, which is twice of that in F2. (3) The extended interfacial-relaxation arc in F2 implies the existence of another interfacial relaxation which becomes observable in F15 by a weak hump (see Fig. 4). One conceivable mechanism of the relaxation might be the Maxwell-Wagner relaxation, as already discussed in superlattice.[13,14] Although the source of the relaxation deserves further investigation, this cannot hinder us to conclude that it is the relaxation that greatly enhances the interfacial polarization thereby elevating f_d to a higher frequency. The frequency dependences of the capacitance for F2 and F15 under different biases shown as insets in Figs. 3 and 4, respectively, further convince this point. From the inset of Fig. 3, we note that at the fixed frequency of 1 MHz, very close to f_d of F2, the capacitance still has visible decrease with increasing dc biases. This is because the interfacial polarization still at

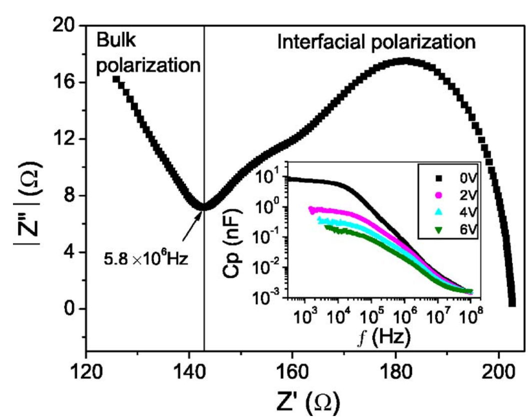

FIG. 4. (Color online) Complex impedance plot of F15. The vertical line indicates the demarking frequency where the polarization changes from interfacial type to bulk type. The inset shows the frequency dependence of the capacitance for F15 under different dc biases.

work at this frequency. While for F15, 1 MHz is far away from the demarking frequency, hence, the film shows remarkable change in capacitance with increasing dc bias, as seen from the inset of Fig. 4. These results suggest that the enhanced voltage tunability in multilayer films is closely related to the enhancement of the interfacial polarization.

To further support the above point, we conducted a quantitative analysis on the interfacial and bulk contributions. The interfacial polarization can be treated as reorientation polarization and the field dependence of the dielectric constant can be written as[19]

$$\varepsilon = a[\cosh(bE)]^{-2}, \quad (1)$$

where a and b are temperature-dependent constants and E is the applied field. While for the bulk contribution, since the pseudocubic lattice parameter of the BTO (4.033 Å) is larger than that of LSMO (3.876 Å), the field dependence of the dielectric constant for the constrained film is given by[20]

$$\varepsilon = 1/\{p + qE^2\}, \quad (2)$$

where p and q are constants.

Considering Eqs. (1) and (2), the analytic result can be compared with the experimental data. The solid curves in Fig. 1 are the analytic results which perfectly fit the data points. The analytic results reveal that the interfacial polarization is suppressed quickly with increasing electric fields and frequencies, confirming that the rapid drop in normalized capacitance at low frequencies is due to the suppression of interfacial polarization. At 1 MHz and $E=45$ kV/cm, the interfacial contributions to the normalized capacitance of F1, F2, and F15 were found to be 1.73%, 1.83%, and 13.62%, respectively. This substantially convinces the considerable enhancement of the interfacial polarization in F15 and therefore the improved tunability can be ascribed to the enhanced interfacial polarization.

In summary, the voltage tunability of BTO single layer and LSMO/BTO multilayer films were investigated in low-frequency range (≤1 MHz). The interfacial polarization was found to play a decisive role on the voltage tunability in the frequency range. In multilayer films, the interfacial polarization, and in turns the tunability, was significantly enhanced by an additional interfacial polarization originating most likely from the Maxwell-Wagner relaxation. It is therefore suggested that the observed dielectric tunability in the frequency range is dominated by the interfacial polarization

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