Microwave-frequency loss and dispersion in ferroelectric $Ba_{0.3}Sr_{0.7}TiO_3$ thin films

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We report on broadband microwave-frequency measurements of epitaxial ferroelectric $Ba_{0.3}Sr_{0.7}TiO_3$ thin films that reveal systematic increases in the loss and dispersion as the frequency increases toward 40 GHz. Our analysis provides evidence that the origin of this increased loss and dispersion is the direct coupling of microwave energy into a broad distribution of damped soft-phonon modes. We believe that nanometer-sized polar regions in the thin films play a role in this process, resulting in lattice-dynamical loss mechanisms that extend several decades in frequency below the frequency of the soft mode in these thin-film materials. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2033139]

High-permittivity ferroelectric thin films are widely being pursued for insertion into key technological areas such as next-generation embedded dynamic random access memories (DRAMs)[1] and electronically tunable communication devices.[2] Despite the imminence of these commercial applications, losses and dispersion at rf and microwave frequencies in thin-film ferroelectrics are poorly characterized and their origins remain unknown.[3] This situation is due in part to the fact that extracting accurate quantitative dielectric properties of thin films at rf and microwave frequencies is a formidable task, and only a handful of reliable techniques exist.[4–6] In order to address this critical issue, we have developed new swept-frequency measurement techniques that accurately determine the complex relative permittivity $\varepsilon_r^*(\omega)=\varepsilon_r'+i\varepsilon_r''$ of thin-film dielectric samples as a continuous function of frequency up to 40 GHz. The frequency dependence of the dielectric response, measured at variable temperatures, provides insight into the origin of losses and dispersion in these materials. Our measurements provide the basis for a new quantitative model for the frequency dependence of the dielectric response of ferroelectric thin films, and our analysis strongly suggests that coupling to a distribution of lattice soft-phonon modes is the dominant loss mechanism in thin-film ferroelectrics at microwave frequencies.

It is well known that ferroelectricity of a material is manifest in its lattice soft-mode behavior.[7] In particular, the low-frequency dielectric response of ferroelectrics is dictated by the Lyddane-Sachs-Teller (LST) relation, which directly connects the static dielectric constant $\varepsilon(0)$ with the frequencies of the transverse optical (TO) and longitudinal optical (LO) phonon modes:[7]

$$\frac{\varepsilon(0)}{\varepsilon(\infty)}=\prod_{j=1}^{N}\frac{\omega_{\mathrm{LO}j}^2}{\omega_{\mathrm{TO}j}^2}, \tag{1}$$

where $\varepsilon(\infty)$ is the high-frequency dielectric constant. Normally the phonon modes other than the lowest transverse optical mode (the soft mode) depend only weakly on the temperature, so Eq. (1) directly connects the temperature dependence of the static permittivity $\varepsilon(0)$ with the temperature dependent soft-mode frequency. For ferroelectrics, the electric-field-induced reduction (tuning) of the dielectric permittivity is associated with the increase in frequency (hardening) of the soft mode,[8] and the high permittivity values that can be obtained in these materials are due to a comparatively low value of ω_{TO1}. These properties make ferroelectric materials attractive for a wide range of electronic applications.

Ferroelectric materials in thin-film form are generally favored for integration into the majority of device applications, but possess properties that can be very different from crystals or bulk ceramics: they exhibit reduced dielectric constant, higher losses, and broader transition behavior in the temperature-dependent permittivity $\varepsilon_r(T)$. Raman measurements of the soft-phonon mode in $SrTiO_3$ (STO) and $Ba_xSr_{1-x}TiO_3$ (BST) thin films have shown that the LST relation holds in thin films,[9–11] but also demonstrate that the soft-mode frequency in films is higher than in crystals, and more susceptible to hardening as a function of temperature or bias field. The dramatic differences in observed properties between thin films and single crystals have recently been attributed by a number of authors[11,12] to the presence of nanometer-sized polar regions in the thin-film samples. These nanopolar regions are believed to be caused by defects, local strain, and other microstructural details specific to the thin-film material system.

The material $Ba_xSr_{1-x}TiO_3$ is one of the most widely studied ferroelectric thin-film systems because of the high dielectric constant that can be obtained. At audio frequencies, measurements of BST thin films show low losses and only very weak dispersion.[1,13] This behavior is characteristic of the static regime: ε_r' decreases only slightly with increasing frequency, while the losses can be quite low and are determined primarily by impurities or defect concentrations. For crystals and bulk ceramics the static regime extends throughout the microwave range, as demonstrated for STO crystals[14] and BST ceramics.[15] For thin films, the experimen-

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tal results indicate some increase in losses and dispersion at microwave frequencies (compared to the static response), although there has been no consensus as to the cause. Dalberth *et al.*[5] have observed a sizable change in dielectric constant and loss tangent at low temperatures in epitaxially grown STO films on $LaAlO_3$ as the measurement frequency is increased from 10 kHz to 1 GHz. Similarly, an increase in the loss tangent has been seen[16] in BST films for increasing frequency up to ~10 GHz. Recently, Hubert *et al.*[12] have used a local optical probe at 1–20 GHz to reveal the existence of mesoscopic microwave dispersion in epitaxial BST films. Due to the ever-increasing operation frequency of computer and communications applications, it is imperative to develop consistent measurements and models of the dielectric response of ferroelectric thin-film materials at frequencies throughout the microwave range.

Attempts to systematically characterize thin dielectric films using traditional microwave-frequency measurements, however, typically encounter a number of technical difficulties. Resonant cavity techniques experience reduced sensitivity due to the small filling fraction of thin films that are often <1 μm in thickness. Measurements of lumped-element devices such as interdigitated or vertical capacitors suffer from the onset of distributed effects at higher frequencies (when the measurement wavelength begins to approach the device dimensions), making it difficult to accurately determine the frequency dependence of the extracted permittivity. To conclusively determine the behavior of thin-film ferroelectrics at rf and microwave frequencies we have developed new swept-frequency measurements of distributed planar structures—coplanar waveguide transmission lines loaded by BST thin films—to obtain the complex relative permittivity $\varepsilon_r^*(\omega)=\varepsilon_r'+i\varepsilon_r''$ of thin-film BST samples over the frequency range 1 MHz to 40 GHz. By focusing on distributed structures, we can push our measurement results to higher frequencies than can be achieved for lumped-element techniques, making it possible to determine the frequency dependence of $\varepsilon_r^*(\omega)$ over the entire microwave range in a single measurement configuration.

Our ferroelectric samples were epitaxial $Ba_{0.3}Sr_{0.7}TiO_3$ thin films 400 nm in thickness made by pulsed laser deposition on $LaAlO_3$ substrates 16×16 mm^2 in area. Interdigitated capacitors (IDCs) and coplanar waveguide (CPW) transmission lines with 1 μm thick silver conductors were patterned onto the film surface using a liftoff technique. To obtain the complex microwave-frequency relative permittivity $\varepsilon_r^*(\omega)$, we measured the complex frequency-dependent propagation constant[17] $\gamma(\omega)$ of broadband CPW transmission lines[18] using a variable-temperature microwave probe station.[19] The capacitance and conductance per unit length were extracted using the method of Ref. 6, and the permittivity was obtained by means of finite element calculations of the specific CPW structures. Measurements of single crystal substrates generally yield frequency-independent value for ε_r^* that are consistent with bulk values. Measurements of CPW lines with gap spacings of 10, 25, and 50 μm (all with 50 μm center conductor linewidths) yield consistent values for ε_r^* for the thin films, indicating that interface effects between the conductor and ferroelectric film do not contribute significantly to the measured response.

Figure 1 shows the measured frequency dependence of the real and imaginary parts of $\varepsilon_r^*(\omega)$ for a $Ba_{0.3}Sr_{0.7}TiO_3$ sample at 235 K (the temperature at which the low-frequency capacitance measured on an IDC structure at 100 kHz is a maximum, identified as the Curie temperature T_c in the inset to Fig. 1). Immediately apparent from Fig. 1 is the strong dispersion and increase in loss that occurs as the frequency increases beyond about 1 GHz. We can fit the frequency dependence of both the real and imaginary parts of the $\varepsilon_r^*(\omega)$ data to the Cole–Cole function:[20]

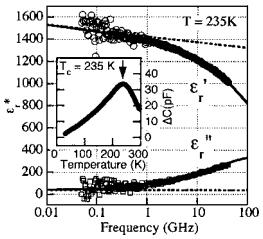

FIG. 1. Complex permittivity $\varepsilon_r^*(\omega)$ for a $Ba_{0.3}Sr_{0.7}TiO_3$ thin film at 235 K. Also shown as solid lines is the fit to the Cole–Cole function. The dashed line shows the modified static permittivity ε_s^*. The inset shows the film capacitance ΔC vs temperature for an interdigitated capacitor at 100 kHz.

$$\varepsilon_r^*(\omega)=\varepsilon_{r,\infty}+\frac{\varepsilon_{r,s}^*-\varepsilon_{r,\infty}}{1+(i\omega\tau)^{\beta}}, \tag{2}$$

where $\varepsilon_{r,\infty}$ is the high-frequency relative permittivity and τ is a characteristic timescale. The exponent β allows for a distribution of characteristic times in the system, and is equal to one for simple Debye-type relaxation. To fit our measured data, we modified the static relative permittivity in Eq. (2) from $\varepsilon_r(0)$ to $\varepsilon_{r,s}^*=\varepsilon_{r,s}'(\omega/\omega_0)^m-i\varepsilon_{r,s}''$ (shown as a dashed line in Fig. 1), in order to account for the weak frequency dependence and finite loss observed experimentally in the permittivity of these materials at lower frequencies (1–100 MHz). The fit shown in Fig. 1 as the solid line uses $\beta=0.58$ and $\tau=0.8$ ps, with $\varepsilon_{r,\infty}=6$, $\varepsilon_{r,s}^*=1651-39i$ at $\omega/2\pi=100$ kHz, and $m=-0.016$. These values for the dispersion parameter m and loss tangent ($\tan\delta=\varepsilon_{r,s}''/\varepsilon_{r,s}'=0.02$ at 100 kHz) are comparable to previously reported values on BST thin films measured at kHz frequencies.[13] Figures 2(a) and 2(b) show similar fits to the frequency-dependent permittivity of the same sample at temperatures above and below T_c, respectively. Although only the real part of the permittivity is shown in Fig. 2, both real and imaginary parts are used in the fitting process.

Fits to the data in Figs. 1 and 2 using the Cole–Cole function allow us to extract the relevant parameters from Eq. (2) as a function of temperature for the $Ba_{0.3}Sr_{0.7}TiO_3$

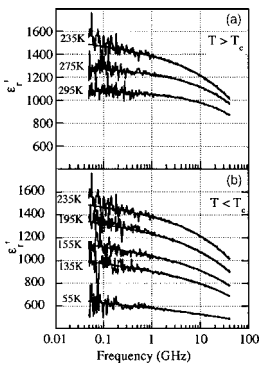

FIG. 2. Measured data and fits for $\varepsilon_r'(\omega)$ for a $Ba_{0.3}Sr_{0.7}TiO_3$ thin film at different temperatures: (a) $T>T_c$; (b) $T<T_c$. The fits include both the real and imaginary parts of the permittivity function.

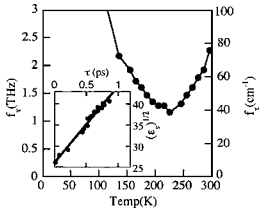

FIG. 3. Temperature dependence of the soft-mode frequency $1/\tau$ extracted from the frequency dependence of $\varepsilon_r^*(\omega)$ for a $Ba_{0.3}Sr_{0.7}TiO_3$ thin film. The inset shows the square root of the static permittivity plotted as a function of the inverse soft-mode frequency.

sample. Figure 3 shows the temperature dependence of the extracted frequency $1/\tau$, which reaches its minimum value at the Curie temperature T_c. We note that $1/\tau$ increases as the temperature moves away from T_c in either direction, which is similar to the behavior of the lattice soft-phonon mode in ferroelectric materials. To further explore this behavior, we plot in the inset to Fig. 3 the square root of the static permittivity (defined as ε_r' at 100 kHz) as a function of the value of τ extracted from our frequency-dependent fits to the complex relative permittivity data in Fig. 2. The resulting linear relationship demonstrates that our characteristic frequency $1/\tau$ obeys the LST relation [Eq. (1)] for different temperatures. Based on these observations, we identify $1/\tau$ extracted from our microwave frequency permittivity measurements with the frequency of the soft-phonon mode. We note that these values for the soft-mode frequency and its behavior as a function of temperature show good agreement with Raman measurements of the soft-mode frequency for similar BST materials over the same temperature range.[11]

The preceding analysis strongly suggests that a significant contribution to the microwave frequency loss and dispersion in thin film BST samples is due to the direct coupling of energy into a broad distribution of soft-phonon modes within the thin-film sample. This is a dynamical process that occurs over several decades in frequency, and is very different from dynamical effects in crystal or bulk ceramic materials, which are typically observed only at much higher frequencies. The β values observed in our samples ($\beta=0.58$ and approximately independent of temperature for the sample in Fig. 2) indicate a relatively broad distribution of soft-mode frequencies, which is likely due to the nanometer-scale inhomogeneity observed in these materials,[21] where each individual region can have its own local soft mode frequency. Our results imply that material optimization resulting in a sharper distribution of phonon frequencies ($\beta->1$) will help reduce losses and dispersion in these materials for frequencies much less than the soft mode frequency ($\omega \ll 1/\tau$).

However, even for a single soft-mode frequency ($\beta=1$), Eq. (2) implies that losses and dispersion due to phonon effects will extend several decades below the soft-mode frequency in these thin film systems. As long as Eq. (2) remains valid, losses will peak at a frequency of $1/(2\pi\tau)$, and the loss tangent will be directly proportional to proximity to soft mode frequency: $\tan\delta=\omega\tau$ (in the limit $\varepsilon_r' \gg \varepsilon_\infty$). Our results therefore expose a direct connection between high permittivity values (and hence also high tuning) in ferroelectric thin-film systems and high microwave loss: high ε_r' values result from a low value of ω_{TO1}, by the LST relation, Eq. (1); however, a low ω_{TO1} also gives high values of $\tan\delta$, by Eq. (2). An immediate practical consequence of these results is the conclusion that improvements in the static dielectric properties of ferroelectric thin films will not necessarily translate into improved performance at microwave frequencies, since the main source of loss and dispersion at microwave frequencies can be due to dynamical effects involving the soft-mode distribution.

In conclusion, we have applied a new measurement technique to characterize the complex permittivity of ferroelectric BST thin-film samples over a broad range of frequencies (10 MHz–40 GHz). Our measurements reveal a strong increase in the losses and dispersion with increasing frequency for these materials, at temperatures in the vicinity of the Curie temperature T_c. We can quantitatively describe our measured $\varepsilon_r^*(\omega)$ data for BST films at different temperatures using a Cole–Cole function with $1/\tau$ given by the soft-mode frequency and exponent β in the range 0.5–0.6. Our analysis indicates that the microwave loss and dispersion observed in these thin-film materials are due to direct coupling of microwave energy into a broad distribution of damped soft-phonon modes within a single thin-film sample. The mechanism responsible for such coupling is likely to be the distribution of nanopolar regions observed in the films, which strongly overdamp the soft-phonon mode. Due to the broad, relaxor-like frequency dependence of $\varepsilon_r^*(\omega)$, the static description of the dielectric permittivity and loss breaks down several orders of magnitude below the soft-mode frequency in these thin-film materials.

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