

Microwave dielectric relaxation of the polycrystalline (Ba,Sr)TiO₃ thin films

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The microwave dielectric properties of the (Ba,Sr)TiO₃ thin films annealed at various oxygen pressures ranging from 5 to 500 mTorr were investigated over the frequency range 0.5–5 GHz using a circular-patch capacitor geometry. The dielectric constant (ϵ) followed Curie–von Schweidler relaxation in the microwave-frequency range, and the degree of relaxation corresponded qualitatively with the measured dielectric loss ($\tan \delta$). As the oxygen pressure varied, the dielectric loss had a maximum value of ~ 0.03 at 100 mTorr, and its behavior was correlated with the Raman strength of the polar modes. © 2005 American Institute of Physics. [DOI: 10.1063/1.1923760]

Recently, (Ba,Sr)TiO₃ thin films have been studied intensively for applications in areas such as dynamic random access memory (DRAM) or microwave devices.^{1–5} Because of the voltage pulse applied in DRAM and the operating microwave frequency of tunable devices, it is important to understand the frequency dependence of the dielectric properties, such as the dielectric constant (ϵ) and dielectric loss ($\tan \delta$) at GHz range.

The existence of a polar nanoregion (PNR) in ferroelectric films has been proposed previously to explain the observation of the first-order Raman scattering and the Fano asymmetry of the Raman lines in the SrTiO₃ films.⁶ Several studies have also shown that PNR, similar to those in a relaxor, exists in BST thin films above the bulk ferroelectric-transition temperatures.^{7–9} Herein, we report the microwave dielectric properties and PNR characteristic of BST thin films.

The BST thin films (~ 350 nm) were deposited on Pt (100 nm)/SiO₂ (100 nm)/Si (100) wafer using a (Ba_{0.5}Sr_{0.5})TiO₃ target by rf magnetron sputtering, at the deposition temperature of 600 °C with the operating pressure of 40 mTorr. The samples were postannealed at 700 °C in a pure-oxygen atmosphere, and the oxygen pressures were varied from 5 to 500 mTorr. The Au thin films (200 nm) as the top electrode were patterned to circular-patch capacitor structures in order to measure the dielectric properties in the microwave range.^{7,10,11}

The dielectric properties were measured using a vector network analyzer (HP 8510C) in the frequency range from 0.5 to 5 GHz. The scattering parameter, S_{11} , of the device under test (DUT) acquired by a one-port measurement technique was converted into the impedance. The dielectric constants and the dielectric losses were obtained from the DUT impedances, the dielectric thicknesses, and the electrode areas. The equivalent-circuit model was introduced to remove the parasitic effects from resistance in the bottom/top electrode and contact.^{7,11} X-ray diffraction (XRD) with Cu $K\alpha$

radiation was used to determine the crystal structures of the thin films. Unpolarized Raman spectra (Jobin Yvon) were acquired with backscattering geometry at room temperature in the range from 100 to 1100 cm⁻¹. The composition of the thin films was analyzed by electron-probe microanalysis (EPMA), and the film thickness was measured using a surface profilometer.

The average composition of the BST thin films was (Ba_{0.44}Sr_{0.56})Ti_{0.91}O_{3- δ} , which was confirmed by EPMA. The Ti deficiency due to the larger solubility than bulk BST, which can be explained by the nonequilibrium microstructures, may contribute only to the overall degradation of dielectric constants and losses compared with the stoichiometric one.^{1,12,13} Figure 1 shows the XRD patterns of the BST thin films annealed at various oxygen pressures. All of the BST films show the polycrystalline (100), (110), and (111) grains in the range from 20° to 60°. In order to examine the extent of the (100) texturing, the (200)/(110) integrated-intensity ratios of the BST thin films were acquired (Fig. 2). The (111) diffraction was precluded due to

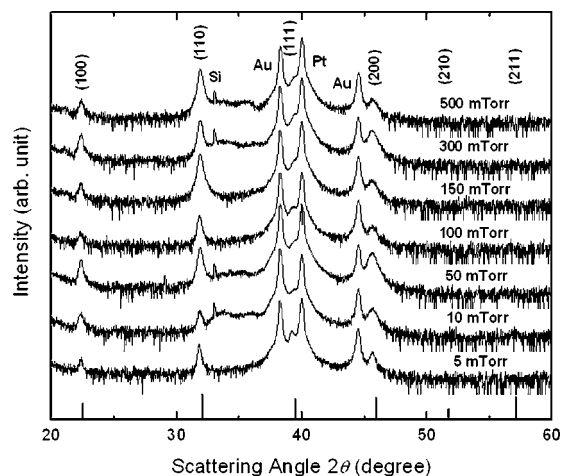


FIG. 1. XRD patterns (in a log scale) of the BST thin films annealed at various oxygen pressures ranging from 5 to 500 mTorr. The peak positions and intensities of the (Ba_{0.5}Sr_{0.5})TiO₃ powder (JCPDS No. 39-1395) are marked at the bottom.

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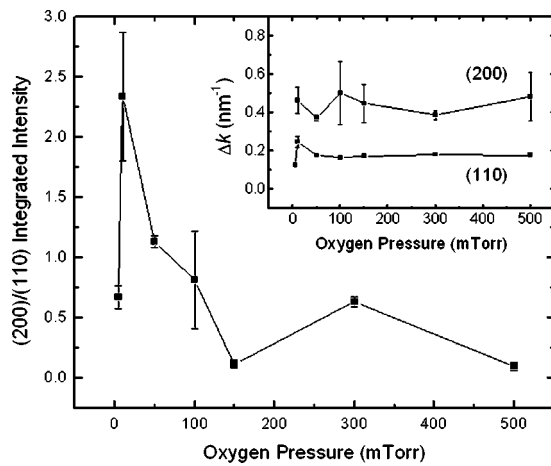


FIG. 2. The (200)/(110) integrated-intensity ratios of the BST thin films annealed at various oxygen pressures. The inset shows the variation in the XRD peak widths Δk (full width at half maximum) of the (200) and (110) diffractions.

overlapping with the electrode peaks.² It is observed that (100) texturing has a maximum value at 10 mTorr. However, the growth kinetics for the preferred orientation as the oxygen pressure varies is not well understood. The XRD peak widths Δk (full width at half maximum) of the (200) and (110) diffractions do not show any consistent changes, as shown in the inset of Fig. 2.

Figure 3 shows the dielectric constant and the dielectric loss of the BST thin film annealed at 10 mTorr as a function of frequency ranging from 0.5 to 5 GHz. The dielectric constant clearly shows a power-law dependence on the frequency, which is known as the Curie-von Schweidler law ($\epsilon \propto f^{-(1-n)}$ with $0 \leq n \leq 1$), and the value of the exponent ($1-n$) means the degree of relaxation in the dielectric constant. The dielectric loss can be approximated to $\cot(n\pi/2)$.¹⁴⁻¹⁶ Figure 4 shows the dielectric constants and the dielectric losses (averaged between 1 and 3 GHz) of the BST thin films annealed at various oxygen pressures (presented by the solid squares). The values of $1-n$ obtained from the least-squares fitting and $\cot(n\pi/2)$ are represented with open circles and open squares, respectively. Figure 4(a) shows that the dielectric constants have a maximum value of ~ 600 at 10 mTorr, which correlates with the (100) texture. It is known that the (100) texture leading to the enhancement of the in-plane oriented polar axis increases the dielectric constant in the BST thin films.² Figure 4(b) shows the qualitative correspondence between the dielectric relaxation ($1-n$

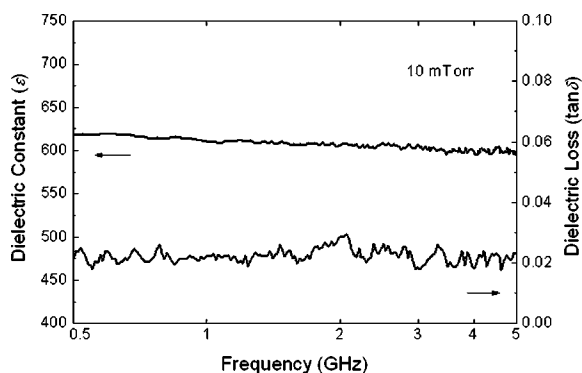


FIG. 3. The dielectric constant (ϵ) and the dielectric loss ($\tan \delta$) of the BST thin film annealed at 10 mTorr in the frequency range from 0.5 to 5 GHz.

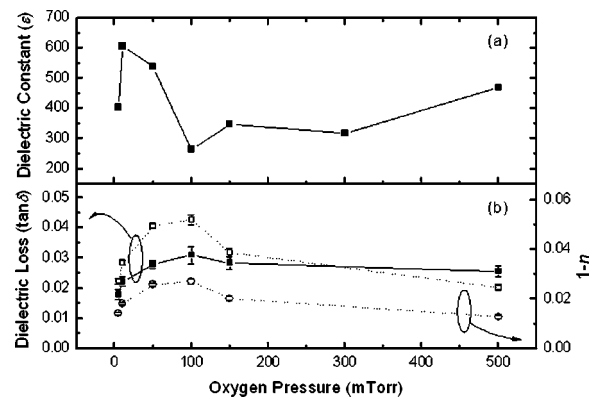


FIG. 4. (a) The dielectric constants and (b) the dielectric losses (averaged between 1 and 3 GHz) of the BST thin films are shown by the solid squares (annealed with various oxygen pressure). The values of the exponent ($1-n$) from the Curie-von Schweidler relaxation law ($\epsilon \propto f^{-(1-n)}$), which were obtained from the least-squares fit, are presented by the open circles. The open squares indicate the calculated dielectric losses using the relation, $\tan \delta \approx \cot(n\pi/2)$.

or $\cot(n\pi/2)$) and the measured dielectric loss ($\tan \delta$). The dielectric loss has a maximum value of ~ 0.03 at 10 mTorr. The dielectric loss means a dynamic dielectric response at the measured frequency. Hubert *et al.*⁸ reported the local ferroelectric (and paraelectric) response of the $(\text{Ba}_{0.4}\text{Sr}_{0.6})\text{TiO}_3$ thin films deposited at various oxygen pressures using time-resolved confocal scanning optical microscopy at microwave frequency. In addition, Raman studies of paraelectric BST thin films have clearly shown the existence of PNR.^{7,9}

The Raman spectra of the BST thin films annealed with various oxygen pressures were obtained, as shown in Fig. 5. The peaks at ~ 180 , ~ 280 , ~ 530 , and $\sim 760 \text{ cm}^{-1}$ are attributed to the mixed transverse optical (TO_2)-longitudinal optical (LO_1), TO_3 - LO_2 , TO_4 , and LO_4 modes, respectively.⁹ The first-order Raman scattering is forbidden because all the zone-center phonon modes have an odd parity in a cubic structure. However, observation of forbidden polar modes in the BST thin films demonstrates the local loss of the inversion center that is assigned to a ferroelectric fluctuation. For the quantitative analysis of the PNR strength, the polar TO_4 and LO_4 modes were fitted with Lorentzian functions after removing the nonlinear background, as shown in the inset of

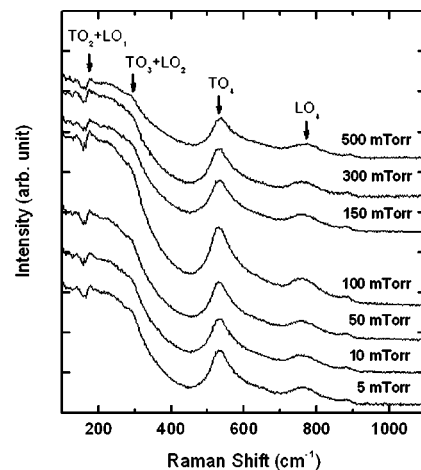


FIG. 5. Raman spectra of the BST thin films annealed at various oxygen pressures ranging from 5 to 500 mTorr.

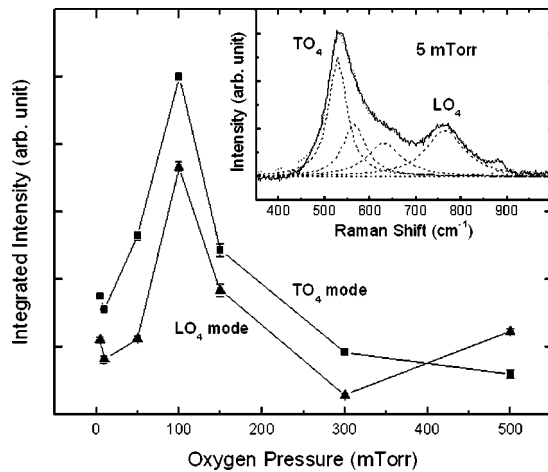


FIG. 6. Integrated intensities of the TO_4 and LO_4 modes of the BST thin films annealed at various oxygen pressures. The Raman peaks are fitted with Lorentzian functions after removing the nonlinear background, as shown in the inset.

Fig. 6. The peaks at $\sim 570\text{ cm}^{-1}$ and $\sim 630\text{ cm}^{-1}$ are the disorder-induced extra bands, and the peak at $\sim 880\text{ cm}^{-1}$ was unidentified.¹⁷ Figure 6 shows the Raman integrated intensity of the BST thin films annealed at various oxygen pressures. Figures 4(b) and 6 show that the microwave loss is well correlated with the Raman integrated intensity of the polar TO_4 and LO_4 modes.

The dielectric dispersion in BST thin films resembles with that of the relaxor. In the relaxor, the formation of PNR is caused by a compositional heterogeneity. In BST thin films, however, the origin of the PNR is known to be an oxygen vacancy (V_O), and the oxygen vacancies connected with locally frozen cation vacancies or impurities can be re-oriented by an external field.^{15,18} The degree of the correlation among the defect dipoles changes Raman intensity of polar modes.⁹ It is believed that the change in the PNR strength is attributed to both the change of the polar axis and the defect concentration. Therefore, the observed microwave loss and dielectric relaxation may be explained by the concentration of oxygen vacancies and the inhomogeneous distribution of oxygen vacancies under the influence of texture and the interaction with biaxial stress.^{5,8} Therefore, it will be more meaningful to quantify the concentration of defects, and thereby correlate it with the dielectric relaxation.

Although typical Curie–von Schweidler relaxation has been reported in several places of literature, the physical origin has not been fully elucidated, due to the existence of controversy.^{8,15,16,19} The frequency dependence of dielectric constant and loss may be caused by competition between nanopolar reorientation and other dielectric origin, such as multiphonon scattering, quasi-Debye mechanism, and acoustic transformation. Actually, Astafiev *et al.*²⁰ showed that the crossover between extrinsic and intrinsic dielectric-loss mechanisms is driven by the dc bias field at microwave frequency. Baniecki *et al.*¹⁶ have showed Curie–von Schweidler relaxation from 1 mHz to 20 GHz for 30 nm BST. The dis-

tribution of either hopping energies or hopping distances of oxygen vacancies leads to such a wide distribution of relaxation times.¹⁵ The wide relaxation time of oxygen vacancies can originate from the interfacial space-charge region or the strain gradient from a substrate.

In conclusion, the dielectric properties of the BST thin films were measured over the frequency range of 0.5–5 GHz using a circular-patch capacitor geometry. The dielectric constant showed Curie–von Schweidler relaxation, and the degree of the relaxation corresponded qualitatively with the dielectric loss. The microwave loss and dielectric relaxation correlated with the PNR strength, as observed by the Raman spectra.

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