Microwave dielectric properties of strained $(Ba_{0.4}Sr_{0.6})TiO_3$ thin films

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Ferroelectric $Ba_{0.4}Sr_{0.6}TiO_3$ (BST) thin films grown on (001) MgO by pulsed laser deposition show a strong correlation between their structure and their microwave dielectric properties. Epitaxially grown BST films are observed by x-ray diffraction to be tetragonally distorted. The oxygen deposition pressure affects the magnitude of the tetragonal distortion (the ratio of in-plane and surface normal lattice parameters, $D=a/c$) of the deposited BST films. D varied from 0.996 to 1.004 at oxygen deposition pressure of 10–800 mTorr. The dielectric properties of BST films measured at microwave frequencies (1–20 GHz) exhibit an oxygen deposition pressure dependent dielectric constant (ϵ=100–600), and quality factor Q (1/tan δ=10–60). The BST film grown at the oxygen deposition pressure of 200 mTorr exhibits the highest figure of merit [% tuning in $\epsilon \times Q_{0V}$, where % tuning is $100\times(\epsilon_0-\epsilon_b)/\epsilon_0$, and ϵ_0 and ϵ_b are dielectric constant at 0 and 80 kV/cm]. This corresponds to the film with the lowest distortion ($D=1.001$). The observed microwave properties of the films are explained by a phenomenological thermodynamic theory based on the strain along in-plane direction of the films.
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I. INTRODUCTION

The large electric field induced change in dielectric constant of ferroelectric materials, such as $(Ba_xSr_{1-x})TiO_3$ $(0\leqslant x\leqslant 1)$, is currently being used to develop a new class low of loss, tunable microwave devices, such as tunable oscillators, delay lines, and phase shifters.[1–6] Currently, tunable microwave devices are based on either p-i-n diodes,[7,8] or ferrites.[9,10] However, each of these technologies has some disadvantages. The semiconducting devices are extremely lossy at frequencies over 2 GHz and high power is needed to operate ferrite based devices. The realization of low loss tunable microwave devices based on ferroelectric thin films will reduce the size and the operating power of devices, which will have a significant impact on both wireless communications and satellite applications. An issue in the fabrication of these devices is maintaining a large change in the dielectric constant of the ferroelectric film while keeping a low dielectric loss at microwave frequencies.

The dielectric properties of thin films are affected by many factors, such as Ba/Sr ratio, grain size, defect chemistry, oxygen vacancies, strain and stress, and dopants.[1,11–13] Though it is difficult to identify a single mechanism responsible for dielectric loss, it is extremely important to correlate loss mechanisms with film properties. A strong relationship between film structure and dielectric properties has been observed in $(Ba_{0.5}Sr_{0.5})TiO_3$ films grown by pulsed laser deposition (PLD) with different oxygen deposition pressures.[1] As-deposited $(Ba_{0.5}Sr_{0.5})TiO_3$ films with the least stress, grown in a relatively low pressure of O_2, exhibited the highest figure of merit (% tuning in $\epsilon\times Q_{0V}$, where Q_{0V} is Q at 0 kV/cm). Normally a high oxygen ambient is used during film growth in PLD to prevent the formation of oxygen vacancies in the oxide films. The lattice of an oxygen deficient perovskite film expands beyond the size reported for the corresponding bulk ceramic.[1,14,15] During heteroepitaxial thin film growth, strain due to the lattice mismatch between the oxygen deficient film and the substrate changes the structure of the film. Furthermore, strain due to the thermal expansion difference between the film and the substrate also alters the structure of the deposited film during cooling from the deposition temperature to room temperature. The resulting strain in the film at room temperature affects the microwave dielectric properties of the films.

In this article, we present systematic studies of the influence of oxygen deposition pressures on the structure and microwave dielectric properties of epitaxial $(Ba_{0.4}Sr_{0.6})TiO_3$ (BST) thin films grown on (001) MgO by PLD. The oxygen vacancies regulated by changing the oxygen deposition pressures are used to control BST film strain. A maximum in the microwave figure of merit is observed from the film with a minimum strain. The strain dependent dielectric constants agree with those calculated from a theory modified from one developed by Devonshire.[16,17]

II. EXPERIMENT

Epitaxial BST films were deposited onto (001) oriented MgO single crystals by PLD. The output from a pulsed KrF excimer laser (2480 Å, 30 ns FWHM) was focused onto a stoichiometric $(Ba_{0.4}Sr_{0.6})TiO_3$ target with energy density of 2 J/cm^2. The oxygen pressure in the deposition chamber was maintained at a fixed value between 10 and 800 mTorr for

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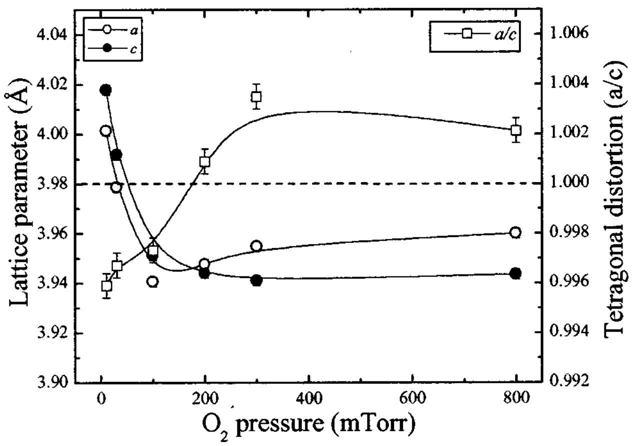

FIG. 1. Oxygen deposition pressure dependent measured lattice parameters along in-plane (a) and surface normal (c) directions of epitaxial $Ba_{0.4}Sr_{0.6}TiO_3$ films on MgO single crystals, and calculated tetragonal distortion ($D=a/c$).

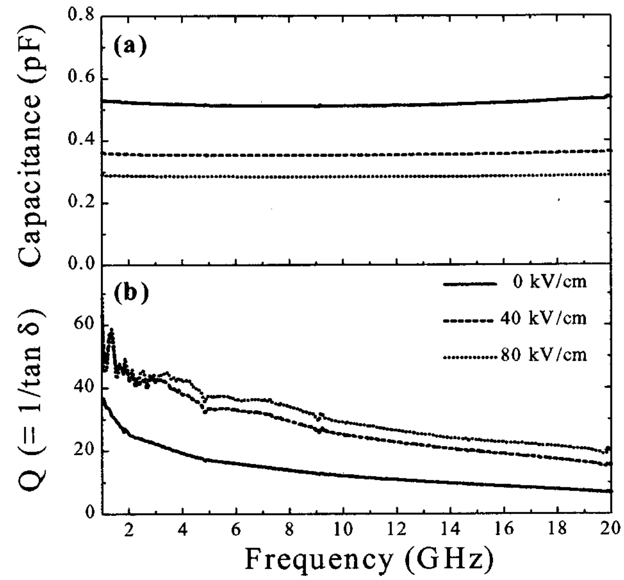

FIG. 2. Typical frequency dependent measured microwave properties, (a) capacitance and (b) quality factor Q of interdigitated capacitor fabricated on BST/MgO.

each deposition, while the substrate temperature was fixed at 750 °C. The thickness of the BST films was ~4000 Å. The lattice parameters of BST films were calculated from the symmetric (002) and (004), and asymmetric (024) and (113) x-ray diffraction peaks measured on a Rigaku rotating anode x-ray diffractometer equipped with Cu $K\alpha$ radiation source and a Huber four-circle diffractometer using Cu $K\alpha_1$ radiation. Diffraction from the MgO substrate was used as an internal standard to reduce errors associated with measurement. In addition, each BST diffraction peak was fitted with Gaussian functions after removing the background. The uncertainty of the lattice parameter is typically less than 0.001 Å. Microwave dielectric properties of the BST films were measured by an HP 8510C network analyzer at 0.1–2.0 GHz using interdigitated capacitors fabricated from depositing Ag/Au electrodes (about 2 μm) deposited by e-beam evaporation through a PMMA liftoff mask. Dielectric constants were extracted using a modified conformal-mapping, partial-capacitance method from measured capacitance and dimensions of the capacitors.[18]

III. RESULTS AND DISCUSSION

The calculated lattice parameters a (along in-plane) and c (along surface normal direction) for BST ($x=0.4$) films grown at oxygen pressures from 10 to 800 mTorr are shown in Fig. 1 with the calculated tetragonal distortion of film ($D=a/c$). The change in the lattice parameters of the films deposited with oxygen pressure between 300 and 800 mTorr are relatively small, however, those deposited at lower oxygen pressure (10–100 mTorr) show a large change. Generally, films deposited at higher oxygen pressures show $a>c(D>1)$, while films deposited at lower oxygen pressures show $a<c(D<1)$. This demonstrates the strong influence of the oxygen deposition pressure on the film structure. It is very interesting to note that the film deposited at 200 mTorr shows a very small deviation from the cubic symmetry ($D=1$) less than 0.1%, while others show large deviations, ranging from 0.2% to 0.4%. The oxygen pressure for the minimum distortion depends on the Ba/Sr ratios (50 mTorr for $x=0.5$, and 200 mTorr for $x=0.4$). Note that the bulk BST ($0\leqslant x\leqslant 0.6$) at room temperature is a cubic ($a=c$, $D=1$). The observed tetragonal distortion of the BST films is a result of stresses caused by lattice mismatch and thermal expansion difference between BST films and MgO substrates, and by oxygen vacancies.[1] It is very important to understand the role of oxygen vacancies in the film. With a constant number of oxygen vacancies in the film, the distortion of BST film should be a constant due to constant stresses generated by a fixed thermal mismatch difference and a fixed lattice mismatch between the substrate and the film. However, the measured strain in the film, which is a strong function of oxygen deposition pressure, indicates a change in the oxygen vacancy concentration. The changes in *a/c* ratio with oxygen pressure could be the result of probability changes in generating oxygen vacancies of $V_O(1/2,1/2,0)$ and $V_O(1/2,0,1/2)$ due to different activation energies.

The frequency dependent dielectric properties [capacitance and quality factor Q ($=1/\tan\delta$) with 0–80 kV/cm of dc bias fields measured at room temperature] of an interdigitated capacitor fabricated on BST film deposited at 200 mTorr oxygen pressure are shown in Fig. 2. As shown in Fig. 2(a), capacitance at microwave frequencies (1–20 GHz) is constant at a given dc bias field. However, quality factor Q is a function of frequency and dc bias field strength as shown in Fig. 2(b). Figure 3 shows the dielectric constant changes of the representative capacitor of each BST film with dc bias field at 10 GHz. The BST films deposited at 200 and 300 mTorr show large dielectric constant changes with dc bias field, while films deposited at low oxygen pressure (less than 100 mTorr) and at high oxygen pressure (800 mTorr) show smaller changes in dielectric constant. In addition hysteresis is observed in the films deposited at 200 and 300 mTorr, though the bulk BST ($x=0.4$) is paraelectric at room tem-

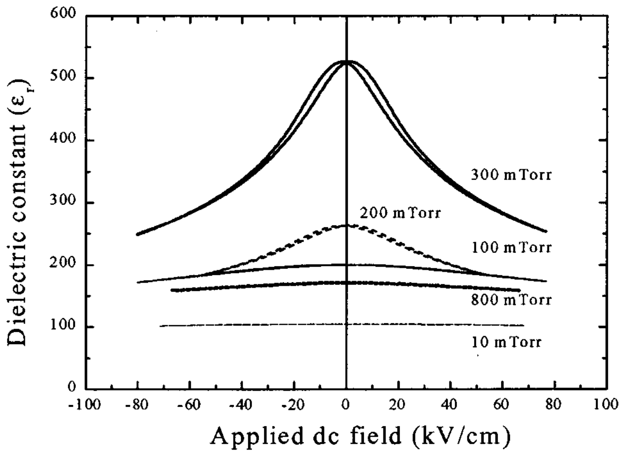

FIG. 3. Dielectric constant changes with applied dc bias fields, which depend on the oxygen deposition pressures.

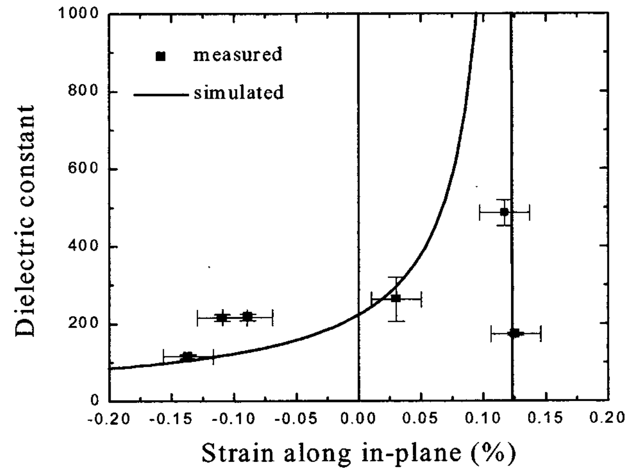

FIG. 5. Measured (square) and theoretically calculated (solid line) dielectric constants of strained BST ($x=0.4$) thin film on MgO.

perature. This suggests that thin epitaxial films have strain induced ferroelectric behavior.

The microwave properties for BST ($x=0.4$) films at 10 GHz as a function of oxygen pressure are shown in Fig. 4: (a) dielectric constant ϵ, (b) % tuning $[100\times(\epsilon_0-\epsilon_b)]/\epsilon_0$, where ϵ_0 and ϵ_b are dielectric constant at 0 and 80 kV/cm, (c) quality factor $Q(=1/\tan\delta)$, and (d) figure of merit K

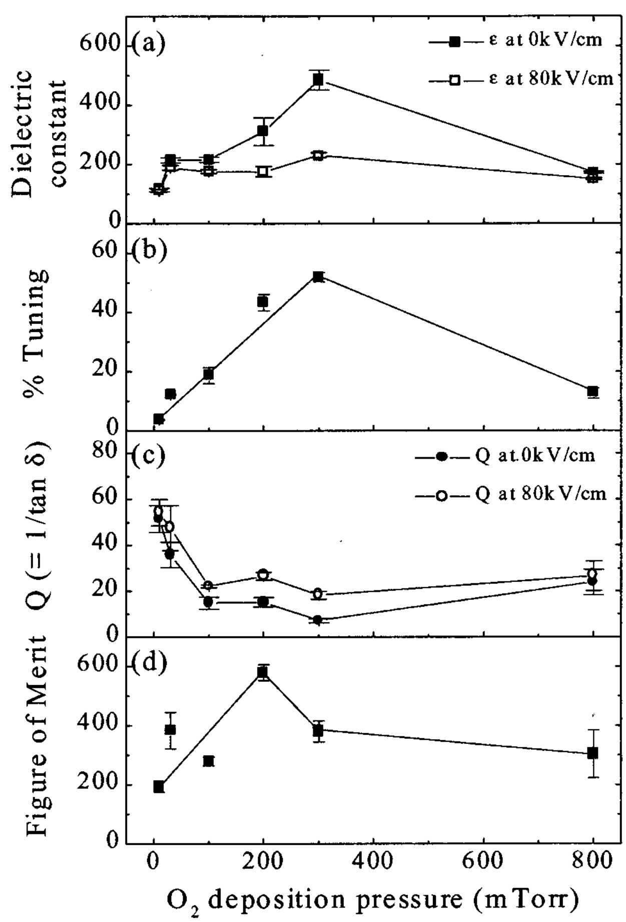

FIG. 4. Oxygen deposition pressure dependent microwave properties of epitaxial BST/MgO: (a) dielectric constant with/without dc bias voltage and (b) dielectric constant % tuning, (c) device Q with/without dc bias voltage, and (d) figure of merit ($K=$% tuning x Q_{0V}).

($=Q_{0V}\times$% tuning, where Q_{0V} is Q at 0 kV/cm). The films grown at lower oxygen pressures (10–30 mTorr) have high Q ($\sim$50), while films deposited at higher pressures (100–800 mTorr) exhibit low Q (10–30). The dielectric constant and % tuning are a maximum at 300 mTorr. Furthermore, the figure of merit of the film with the minimum stress ($D=1.0004$) grown at 200 mTorr shows a maximum value of $\sim$700. These trends in microwave properties of BST films ($x=0.4$) agree with those observed from BST films ($x=0.5$).[1]

The strain effect on the dielectric constant of ferroelectric films were recently reported by Chang *et al.*[13] modified from a phenomenological thermodynamic theory of bulk ferroelectrics developed by Devonshire.[16,17] The dielectric constant of strained films can be expressed as:

$$\partial E/\partial P=1/\epsilon=\alpha+3\beta E^2\epsilon^2+b_1(S)+b_2(E), \tag{1}$$

where α and β are expansion coefficients, S is in-plane strain, $b_1(S)$ is $2G_{11}S+2G_{12}[1-2(c_{12}/c_{11})]S$, and $b_2(E)$ is $2G_{11}R_{11}E^2+2G_{12}[1-2(c_{12}/c_{11})]R_{11}E^2$, c_{ij}, G_{ij}, and R_{ij} are the elastic constants, the stress-polarization related electrostrictive coefficients, and the strain-electric field related electrostriction coefficients, respectively, and E is the applied dc electric field. The strain along in-plane of the BST ($x=0.4$) can be calculated from measured a and c by following,

$$S=(a-a_0)/a_0,$$

where $a_0=(a\times a\times c)^{1/3}$. Figure 5 shows the relationship between the calculated strain S of BST ($x=0.4$) on MgO and the measured dielectric constant. The measured dielectric constant increases gradually as the strain goes from compressive strain (-0.14%) to tensile strain (0.12%). The change of the dielectric constant with in-plane strain agrees with the theory (solid curve in Fig. 5) at $E=0$ with $\epsilon_0=200$, where ϵ_0 is a dielectric constant extrapolated at $S=0$. When the right-hand side term of Eq. (1) is 0, the dielectric constant ϵ is infinite. There is a large change in measured dielectric constants near $S\approx0.12\%$, which may correspond to a paraelectric–ferroelectric phase transition caused by a strain larger than 0.12%. Theoretically, the strain dependence of the dielectric constant will be divergent at the critical strain corresponding to a paraelectric–ferroelectric phase transition. However, the measured dielectric constant does not diverge due to strain relaxation through the thickness of the film and local compositional inhomogeneities of the film, which reduces the dielectric constant of the film near the critical strain.

IV. SUMMARY

In summary, we report a strong correlation between the microwave dielectric property and the structure of the epitaxial BST films grown on (001) MgO single crystal substrate by PLD. Strain in the film affects the dielectric constant of BST films. The relation between measured dielectric constants and measured strains qualitatively agrees with the theoretical description developed by Devonshire. The studies of BST thin films with $x=0.4$ show a clear relationship between structure and dielectric properties at microwave frequencies. First, dielectric constant and % tuning are maximum for the film with near zero strain. Second, high Q's (low loss) are observed films deposited at very low oxygen pressures (less than 30 mTorr). Third, the microwave figure of merit is maximum when film stress is a minimum.

ACKNOWLEDGMENTS

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