

Microwave properties of tetragonally distorted $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ thin films

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A strong correlation is observed between the structure and the microwave dielectric properties of epitaxial $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ (BST) thin films deposited onto (001) MgO by pulsed laser deposition. Films were deposited at 750 °C in an oxygen pressure that was varied from 3 to 1000 mTorr. The tetragonal distortion (ratio of in-plane and surface normal lattice parameters, $D = a/c$) of the films depends on the oxygen deposition pressure. D varied from 0.996 at 3 mTorr to 1.003 at 800 mTorr. At microwave frequencies (1–20 GHz), BST films with low distortion have higher dielectric constants ($\epsilon \sim 500$), and lower dielectric loss ($\tan \delta \sim 0.02$) compared to films with higher distortion. The correlation of the microwave properties with the film structure can be attributed to stresses and polarizability in the film. The BST film grown at the oxygen deposition pressure of 50 mTorr exhibits a large dielectric constant change and a low dielectric loss at the same time, which corresponds to the film in low stress ($D = 1.0004$). For tunable microwave applications, BST films with low stress are desirable in order to achieve both low dielectric loss and large tunability.
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$(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ (BST) thin films are being used to develop a new class of tunable microwave devices, such as tunable oscillators, delay lines, and phase shifters.^{1,2} These devices are based on the large electric field dependent dielectric constant observed in ferroelectric materials. BST films have been deposited by chemical vapor deposition,³ sputterings,^{4,5} and pulsed laser deposition (PLD).^{1,6–10} PLD provides unique advantages for multicomponent oxide films because it easily reproduces the stoichiometry of the target in the deposited film. Though the oxygen ambient is used to prevent the formation of oxygen vacancies in the deposited film, it has been shown that oxide films grown using PLD are still oxygen deficient.^{7–10} The lattice of an oxygen deficient film expands beyond the size reported for corresponding bulk ceramics.^{8–10} In addition, other factors such as the lattice mismatch and the thermal expansion difference between the film and the substrate alter the structure of the deposited film.¹⁰ An increase in the number of oxygen vacancies in the film increases the lattice parameter of the oxide thin films,^{8–10} but there have been no systematic studies on the influence of oxygen vacancies on the microwave properties of BST films. In this letter, we present systematic studies of the effect of the oxygen deposition pressures on the structure and microwave dielectric properties of epitaxial BST thin films grown on (001) MgO by PLD.

Epitaxial BST films (300 nm) were deposited onto (001) MgO single crystals by PLD. The output of a short pulse excimer laser [248 nm, 30 ns full width at half maximum (FWHM)] was focused onto a stoichiometric $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ target with energy density of 2 J/cm². The oxygen pressure in the deposition chamber was varied from 3 to 1000 mTorr, while the substrate temperature was maintained at 750 °C.

Microwave properties of the BST films were measured by a HP 8510C network analyzer at 0.1–20 GHz range using interdigitated capacitors fabricated from depositing a thick Au/Ag electrode (about 1.5 μm) grown by *e*-beam evaporation.¹¹ The dielectric constant was extracted using a modified conformal-mapping partial-capacitance method using the dimension of the capacitors.^{1,12}

The lattice parameters of BST films were calculated from the symmetric (002) and (004), and asymmetric (024) and (113) x-ray diffraction (XRD) 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. The uncertainty of the lattice parameter is typically less than 0.001 Å.

Figure 1 shows symmetric (002) and asymmetric (024) XRD scans for BST films on MgO. The peak positions of the (002) and (024) MgO are used as an internal calibration for 2θ . The peak positions of the BST films are shifted to a lower angle than those of the reported bulk ceramic, indicating that the lattice parameter of the BST films is larger than that of the bulk [$a_b = 3.9471$ Å for $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$].¹³ Films deposited at lower oxygen pressures show larger peak position shifts, suggesting the strong influence of oxygen pressure. The calculated lattice parameters for films grown at oxygen pressures from 3 to 1000 mTorr are shown in Fig. 2(a). The change in the lattice parameters of the films deposited with oxygen pressure between 350 and 1000 mTorr are relatively small, however, those deposited at lower oxygen pressure (3–50 mTorr) show large changes along both in-plane (*a*) and surface normal (*c*) directions associated with the change in the deposition pressure. The calculated tetragonal distortion of film ($D = a/c$) strongly depends on the oxygen deposition pressure [note that bulk $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ at room temperature is cubic ($D_{\text{bulk}} = 1$)]. At 3 mTorr, D is 0.996 less than 1 ($c > a$). The deposited film is nearly cubic

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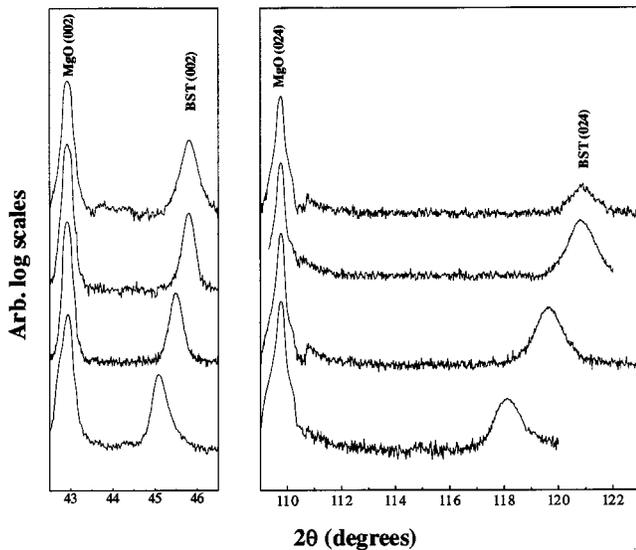


FIG. 1. XRD patterns of symmetric (002) and asymmetric (024) peaks of BST on MgO with different oxygen deposition pressures (3, 50, 350, and 800 mTorr from bottom to top).

around 50 mTorr ($D=1.0004$). D increases monotonically with increasing oxygen pressure to a maximum at 800 mTorr ($D_{800}=1.003$). The film deposited at 50 mTorr shows very small deviations from the cubic symmetry, less than 0.05%, while others show large deviations, ranging from 0.2% to 0.4%. However, the unit cell volume of the film deposited at 50 mTorr is still significantly larger than that of the bulk ($v_{50} > v_{\text{bulk}}$), indicating the film contains a large number of oxygen vacancies.

The influence of oxygen pressure on the volume of the unit cell (v) can be estimated by assuming that oxygen atoms in the BST film and in the chamber are in equilibrium at a given deposition temperature (750 °C). The formation of oxygen vacancies in the film can be represented by

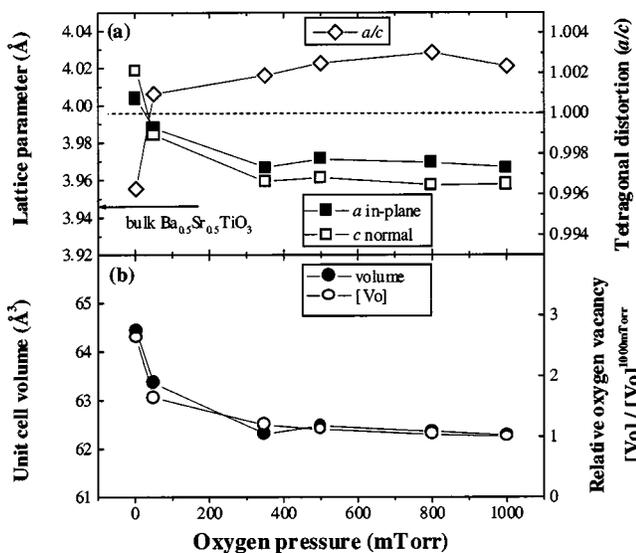
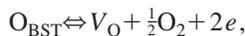


FIG. 2. (a) In-plane (a) and surface normal (c) lattice parameters and tetragonal distortions (a/c) of epitaxial BST film on (001) MgO. (b) Measured volume of the unit cell (v) and estimated relative oxygen vacancy concentration ($[V_{\text{O}}]/[V_{\text{O}}]^{1000 \text{ mTorr}}$).

where O_{BST} is oxygen in BST, and V_{O} is oxygen vacancy in BST. From a simple mass-action equation, the oxygen concentration will be expressed by

$$[V_{\text{O}}][e]^2 \propto \exp(-\Delta H/kT) P_{\text{O}_2}^{-1/2},$$

where $[V_{\text{O}}]$ is the concentration of oxygen vacancies, ΔH is enthalpy for generating oxygen vacancies, and P_{O_2} is pressure of oxygen in the chamber. $[\text{O}_{\text{BST}}]$ is constant because of the relatively small number of oxygen vacancies in the BST matrix. Based on the assumption that $[V_{\text{O}}]$ is $1/2[e]$, the concentration of the oxygen vacancies at constant T is

$$[V_{\text{O}}] \propto P_{\text{O}_2}^{-1/6}.$$

Oxygen vacancies affect the nearest neighbor distance by reducing the Coulomb attractive force between cation and anion atoms, resulting in an increased lattice parameter and unit cell volume. The volume of the unit cell (v) and the relative oxygen vacancy concentration ($[V_{\text{O}}]/[V_{\text{O}}]^{1000 \text{ mTorr}}$) shows a very similar tendency with oxygen pressure in the chamber [Fig. 2(b)]. This agreement confirms that films deposited at low oxygen pressures have more oxygen vacancies than those deposited at higher oxygen pressures. Furthermore, the unit cell volume of the film is a good measure of the relative oxygen vacancy concentration in the film.

The lattice parameter and the tetragonal distortion changes of the films can be explained by both the lattice mismatch and the thermal expansion difference between the film and the substrate, and the number of oxygen vacancies. At the deposition temperature (750 °C), the BST lattice in low oxygen partial pressure will expand beyond that of the corresponding bulk due to the presence of oxygen vacancies. During film growth, the expanded BST lattice will distort and expand along the in-plane direction due to the larger MgO lattice ($a=4.2113 \text{ \AA}$), resulting in a tetragonally distorted BST lattice. During cooling to room temperature, the BST film will experience a compressive stress due to thermal expansion coefficient differences between the BST film and the MgO substrate.¹⁰ The observed tetragonal distortion change from $a/c > 1$ over 350 mTorr to $a/c < 1$ below 3 mTorr and the monotonic increase in the unit cell volume with decreasing oxygen pressure could be the result of the change between stress due to lattice mismatch, thermal contraction difference, oxygen vacancies, and attractive force among atoms in the film. However, these cannot explain that the stress change from tensile to compressive with decreasing oxygen deposition pressures. One possible explanation is that the nonisotropic stresses caused by lattice mismatch between the substrate and the film during deposition may distinguish two crystallographically different oxygen vacancy sites (0, 1/2, 1/2) and (1/2, 1/2, 0) like those in PbTiO_3 [$V_{\text{O}}(1/2,1/2,0)$ is more stable than $V_{\text{O}}(0,1/2,1/2)$].¹⁴ The change of preferential oxygen vacancy sites in the BST film may occur around the oxygen pressure of 50 mTorr based on the observed lattice parameter changes. Films deposited at lower oxygen pressure (< 3 mTorr) may be transformed to the ferroelectric phase due to the induced stresses.¹⁵ The ferroelectric phase, BaTiO_3 , has $a/c \sim 0.989$ which is slightly smaller than 0.996 of the BST film deposited at 3 mTorr oxygen pressure.

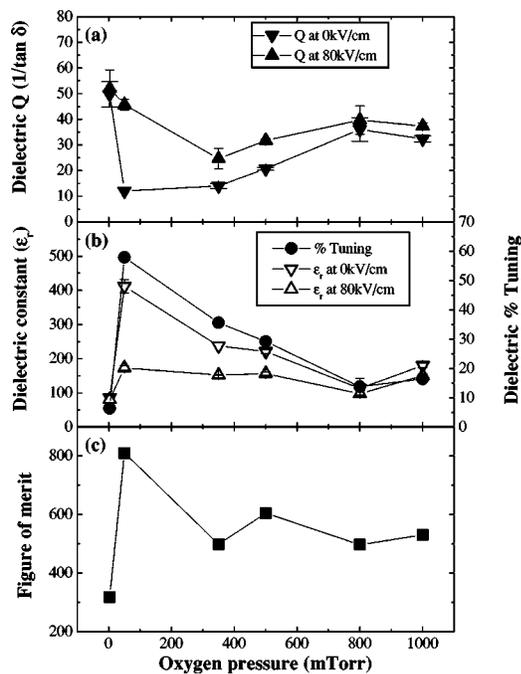


FIG. 3. The dielectric properties of the BST film at 10 GHz; (a) dielectric quality factor $Q (= 1/\tan \delta)$, (b) dielectric constant and its percent tuning, and (c) figure of merit ($= Q_{0 \text{ kV/cm}} \times \% \text{ tuning}$).

The dielectric properties at 10 GHz for BST films on MgO grown at different oxygen pressures are shown in Fig. 3 [(a) quality factor $Q (= 1/\tan \delta)$, (b) dielectric constant and dielectric constant percent tuning with applied dc field of 80 kV/cm, and (c) figure of merit $K (= Q_{0 \text{ kV/cm}} \times \% \text{ tuning})$]. Films grown at 3 and 50 mTorr oxygen pressure have a high dielectric Q (~ 50). From 350 to 1000 mTorr of oxygen, the dielectric Q increases monotonically with increasing oxygen deposition pressure. The dielectric constant and its percent tuning are a maximum at 50 mTorr, which coincides with the minimum in the film stress ($D = 1.0004$). As the oxygen deposition pressure decreases from 1000 to 50 mTorr, the dielectric constant and tunability increase monotonically. Further, the figure of merit of the film with the minimum stress (at 50 mTorr) shows a maximum value ~ 700 . It is very important to note that the film with minimal deviation from the cubic symmetry shows the highest quality factor.

It has been suggested that films in tensile stress have a larger dielectric constant than that in compressive stress.^{16–18} This explains that the change in the dielectric constant for films in tensile stress ($a > c$) and in compressive stress ($c > a$). In addition to this, the number of oxygen vacancies and the unit cell volume plays important roles in determining the dielectric properties of the film. An increased number of oxygen vacancies increases the total polarizability by increasing the number of defect dipoles¹⁴ and the ionic polarizability. The number of defect dipoles increases with an increase in the number of dipoles associated with oxygen vacancies. The ionic polarizability increases with the increased unit cell volume. This explanation is consistent with the observation that the dielectric constant shows increase in the number of oxygen vacancies in the films as oxygen deposition pressures decrease from 1000 to 50 mTorr. These films

show an increase in tunability with increasing oxygen vacancies (decreasing oxygen deposition pressure). BST films grown at 50 mTorr, which is in minimal stress, shows an increased polarizability, and exhibits low dielectric loss (high Q) and high tunability. This strongly suggests that films with low stress are highly desirable for tunable microwave device applications.

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. The BST films on MgO show different types of tetragonal distortion; $c > a$ at low oxygen deposition pressure (≤ 3 mTorr), $c \approx a$ at 50 mTorr, and $a > c$ at high pressure ($350 < P_{O_2} < 1000$ mTorr). The observed change in the unit cell volume agrees well with the predicted change of the relative oxygen vacancy concentration calculated by the mass-action equation. The microwave properties are strongly correlated with the tetragonal distortions and unit cell volumes: (1) dielectric constant tuning and dielectric Q increase with increasing unit cell volume and number of oxygen vacancies and (2) stress change from tensile to compressive decrease dielectric constant of BST films deposited at low oxygen pressure (< 3 mTorr). It is important to note that the film with low tetragonal distortion (close to the cubic symmetry) has a high dielectric constant, large tunability, high dielectric Q , and high figure of merit. This shows, clearly, that for tunable microwave application BST films with low stress or strain are required.

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