Epitaxial growth and planar dielectric properties of compositionally graded $(Ba_{1-x}Sr_x)TiO_3$ thin films prepared by pulsed-laser deposition

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We have heteroepitaxially deposited compositionally graded $(Ba_{1-x}Sr_x)TiO_3$ (BST) thin films with increasing x from 0.0 to 0.25 on (100)-oriented MgO substrates using pulsed-laser deposition. The compositional gradients along the depth in the graded films were characterized by Rutherford backscattering spectroscopy. By using surface interdigital electrodes, the planar dielectric response of epitaxial graded BST films was measured as a function of frequency, temperature, and dc applied voltage. At room temperature, the dielectric constant of the graded BST film was about 450 with a dielectric loss, $\tan\delta$ of 0.007 at 100 kHz. Measurements varying the dc bias voltage showed hysteresis of the dielectric response and a tunability of 25% at an applied electric field of 80 kV/cm. The graded BST films undergo a diffuse phase transition with a broad and flat profile of the capacitance versus temperature. Such behavior of the dielectric response in graded BST films is attributed to the presence of the compositional and/or residual strain gradients in the epitaxial graded films. With such a graded structure, it is possible to a build a dielectric thin-film capacitor with a low-temperature dependence of the capacitor over a broad temperature regime. [DOI: 10.1063/1.1475367]

$(Ba_{1-x}Sr_x)TiO_3$ (BST) ferroelectric thin films exhibit a larger electric field dependent dielectric constant, and have attracted considerable attention for applications in active microwave electronics such as microwave phase shifters, frequency agile filters, and tunable high-Q resonators.[1–3] Presently, for tunable device applications, coplanar electrode configurations are frequently used in tunable microwave devices that utilize ferroelectric films. The coplanar tuning configurations are more compatible with planar microwave circuitry because they are readily designed to have capacitance values that provide good impedance matching to the rest of the circuit.[4] However, there is a concern in the practical applications of tunable microwave resonators based on a single composition of BST films that the resonant frequency depends strongly on the temperature changes because the dielectric constant (ε_r) of a single compositional BST film (e.g. $Ba_{0.5}Sr_{0.5}TiO_3$) is highly temperature dependent. Such poor temperature stability of the resonant frequency would result in the carrier signal drifting in and out of resonance on hot and cold days.[5] It would therefore be important to compensate its temperature coefficient of dielectric constant (TCK) without decreasing its high ε_r. To do so, we have developed compositionally graded BST thin films, in which the Curie temperature is tailored by the compositional gradients to meet the requirements of low TCK value and high ε_r dielectric. Such graded materials are highly preferred in the applications where the capacitance of a device should only be weakly dependent on temperature. Furthermore, for the microwave dielectric applications, oriented grain or epitaxially grown films are also highly required. In this work, we report on the epitaxial growth of compositionally graded BST films with increasing x from 0.0 to 0.25, which were deposited directly on MgO (100) single-crystal substrates by pulsed-laser ablation. The planar dielectric properties of epitaxial graded BST films were also measured through surface interdigital electrodes (IDEs) as a function of frequency, temperature, and applied dc bias.

The compositionally graded BST thin films were grown layer by layer on MgO (100) single-crystal substrates by pulsed-laser deposition (PLD). The PLD system used to grow graded BST films has been described previously in more detail.[6] The stoichiometric sintered ceramic targets of $BaTiO_3$, $Ba_{0.9}Sr_{0.1}TiO_3$, $Ba_{0.8}Sr_{0.2}TiO_3$, and $Ba_{0.75}Sr_{0.25}TiO_3$ were used in this work for the film deposition. The graded BST films with a bottom layer of pure $BaTiO_3$ and a surface layer of $Ba_{0.75}Sr_{0.25}TiO_3$ were grown on MgO (100) single crystals at 700 °C in an oxygen ambient pressure of 200 mTorr to a total film thickness of 450 nm. After deposition, the graded BST films were *in situ* annealed at 700 °C for 30 min, and then cooled down to room temperature.

X-ray diffraction indicated that only the (h00) peaks of graded BST films were observed, suggesting a (100)-

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preferred growth orientation. Rocking curve and ϕ scans were also used to examine the misalignment of the lattice and epitaxial growth of BST graded thin films. The results showed that the full width half maximum of BST (200) rocking curve was 0.41°, and the requisite four-fold symmetry was also observed in the scans of the off-axis (220) planes in the graded BST crystal lattice, indicating that the graded films were grown epitaxially on MgO (100) substrates. Atomic force microscopy was also used to analyze the surface morphology of the graded films. A columnar grain structure was observed. The mean size of the grains was 100 nm, and the root-mean-square surface roughness was in 3–8 nm range. The compositional gradients in the film thickness direction were examined by Rutherford backscattering spectroscopy (RBS).

The planar dielectric properties of the graded films were measured by using IDEs technique. The IDEs were patterned by conventional photolithography. A 100 nm-thick Cr/Au bilayer was deposited on the surface of the graded BST films by magnetron sputtering. The IDEs were formed after standard lift-off techniques. The coplanar capacitor consists of 80 pairs fingers that are 1.5 mm long, 10 μm wide, and space 5 μm apart. Electrical connection to a Hewlett Packard HP 4194A test fixture was made by using coaxial tables. The frequency response of the graded BST films was characterized at room temperature, in the frequency range of 10^2–10^7 Hz by a HP 4194A impedance analyzer by applying a small signal of 100 mV amplitude. The dielectric constant of the graded films was extracted from the capacitance using the conformal mapping technique.[7] Temperature dependence of the planar dielectric properties was measured by placing samples in a closed-cycle refrigerator. The measurements were carried out on automated system, whereby a HP 4194A impedance analyzer and the temperature-control box were controlled by a computer. The experimental data were collected continuously at frequency between 10^3 and 10^6 Hz. The temperature range was between −20 °C and 130 °C, and the maximum rate of cooling the samples was less than 1 °C/min. The capacitance–voltage (C–V) measurement was performed at room temperature by applying a small signal of 100 mV and 1 MHz frequency across the sample while the dc bias voltage was swept from a negative bias to positive bias. The dielectric tunability was deduced from the C–V characteristics.

The compositional gradient in the graded BST thin film characterized by RBS is shown in Fig. 1. The RBS spectrum shown in Fig. 1 was measured with a 2.9 MeV He^+ ion beam at a tilt of 5° and a scattering angle of 170°. As shown in Fig. 1, the RBS data clearly confirmed the expected increasing Ba content and the decreasing Sr content toward the bottom of the graded film, which in the graded structure is pure $BaTiO_3$. The measured compositional gradients of Ba and Sr elements in the graded films along the thickness direction were consistent with that of stoichiometric ceramic targets during laser ablation. The thickness of the graded thin film determined by RBS data was also in agreement with that obtained from cross sectional scanning electron microscopy images.

The frequency response of the graded BST films deposited on a MgO (100) substrate is shown in Fig. 2. It can be seen that the measured capacitance exhibited minimal dispersion as a function of the frequency. Using the conformal mapping technique, the dielectric constant (ε_r) at 100 kHz of the graded films was calculated to about 450. The dielectric loss (tan δ) showed no noticeable dispersion at frequencies up to 1 MHz. The loss tangent at 100 kHz was about 0.007. The temperature dependence of the dielectric constant of the graded BST film is shown in Fig. 3. A broadening transition peak at about 90 °C was observed, that corresponds to the tetragonal-cubic phase transition. The maximum temperature, where the value is frequency dependent in the frequency range of 10^3–10^6 Hz, shifts toward higher temperature with increasing frequency. The broadening and flattening of the peak is typical of diffuse transitions as observed in some polycrystalline BST and $BaTiO_3$ thin films.[8,9] In addition, the profile of the dielectric constant versus temperature for the graded BST film experienced linear characteristics with a slope of 1.57/K in the temperature range from −20 °C to 90 °C. Furthermore, the slope value could be tailored by changing the volume fraction of each layer. The inset in Fig. 3 is the corresponding relative change of ε_r, with respect to temperature of the graded thin film. As can be seen in Fig. 3 with such a graded structure, it is possible to build a dielectric thin-film capacitor with a low-temperature dependence of the capacitor over a broad temperature regime. The feature of the flat profile of the dielectric constant

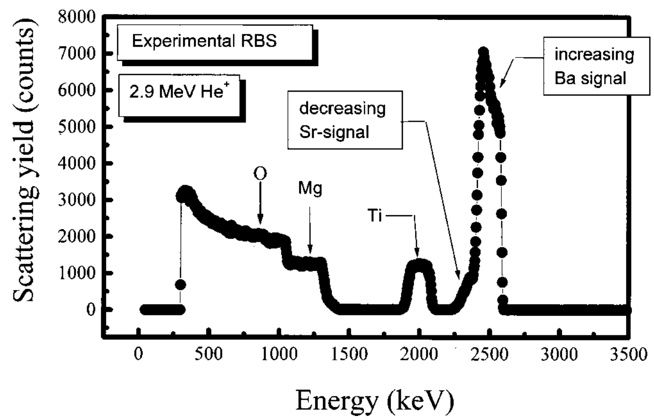

FIG. 1. RBS spectrum of graded BST thin film deposited on a MgO (100) substrate. The composition of the bottom layer is pure $BaTiO_3$.

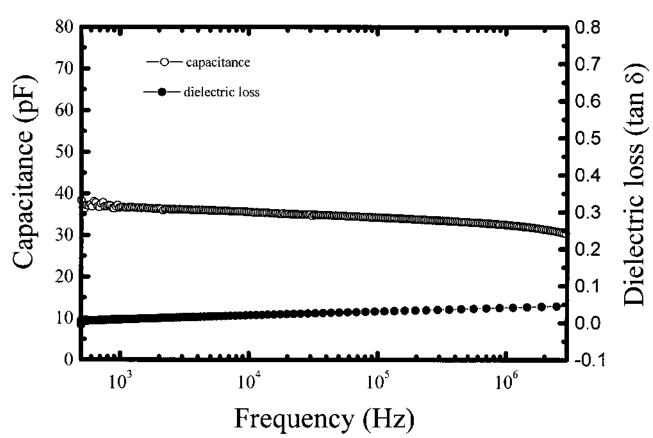

FIG. 2. Variation of the coplanar capacitance and dielectric loss tangent of graded BST thin film deposited on a MgO (100) substrate as a function of the measured frequency. The measurement was performed on 80 pairs fingers of IDEs.

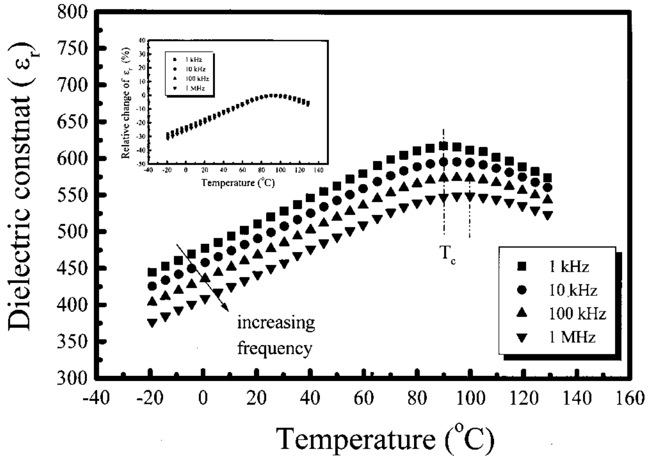

FIG. 3. Temperature dependence of the coplanar dielectric constant, ε_r of graded BST films measured at different frequencies. Inset is the corresponding relative change of dielectric constant with respect to temperature of the graded thin film.

versus temperature for graded BST thin films may be explained by the presence of the compositional and/or residual strain gradients in the epitaxial film as a result of the partial coherence of the film with the substrate.[10] Figure 4 shows the capacitance versus surface electric-field characteristics for graded BST thin film deposited on a MgO (100) substrate. The measurement was carried out at room temperature and 1 MHz. The dielectric constant at zero bias was calculated to be 440, and a decrease in the dielectric constant from ~440 to ~330 was observed with increasing dc bias voltage. Thus, an applied field of 80 kV/cm results in a tunability of 25%. This value is comparable to that of polycrystalline BST thin films[11] (reported to be 25% at an applied electric field of 50–100 kV/cm), and to that of epitaxial $BaTiO_3$ thin films (30% at the field of ~70 kV/cm),[12] but it is smaller than that reported by Carlson *et al.*[13] [about 50%–60% of annealed epitaxial $(Ba_{0.4}Sr_{0.6})TiO_3$ film at 260 K and a field of 57 kV/cm]. The main reason is that the epitaxial $(Ba_{0.4}Sr_{0.6})TiO_3$ film reported by Carlson *et al.*[13] was *ex situ* postannealed at high temperatures of ~1100 °C in a quartz tube furnace under flowing O_2 at pressure of 50–100 mTorr, and such a high temperature postanneal treatment would be beneficial to improving the grain size[14] and crystallinity[15] of

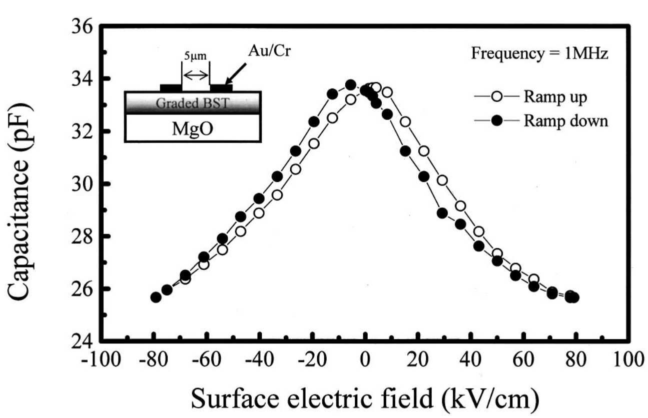

FIG. 4. Variation of capacitance of graded BST films as a function of surface electric field at room temperature and 1 MHz. The measurement was performed on 80 pairs fingers of IDEs.

the film. The present data are only from the preliminary test for the graded films. Improvements in the film quality by optimizing the PLD processing parameters are expected to increase the dielectric properties, and the design of the graded film with layers of high Sr contents would exhibit an essentially broader plateau region of the dielectric constant maximum than the isotropic thin films. Impedance-bias measurements also show hysteresis indicating that the graded films are ferroelectric.

In conclusion, compositionally graded BST films were epitaxially deposited layer by layer on a MgO (100) substrate by PLD. The compositional gradients in the graded BST thin films along the depth were examined by RBS. The dielectric response of the epitaxial graded BST films was characterized by surface IDEs as a function of frequency, temperature, and applied dc bias. The dielectric constant at room temperature was about 450 with a dielectric loss, tan δ, of 0.007 at 100 kHz. An applied electric field of 80 kV/cm resulted in a 25% modulation of the dielectric constant. A broad and flat profile of dielectric constant versus temperature was observed in graded BST films. Such dielectric behavior can be attributed to the presence of the compositional and/or strain gradients in the epitaxial graded films.

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[1] J. P. Goot, S. Trolier-McKinstry, and D. G. Schlom, *Proceedings of the Tenth IEEE International Symposium on Applications of Ferroelectrics, ISAF'96*, 1996, Vol. 1, p. 333.
[2] V. K. Varadan, D. K. Gohdgaonkar, V. V. Varadan, J. F. Kelly, and P. Glikerdas, J. Microwave **35**, 116 (1992).
[3] F. A. Miranda, R. R. Romanofsky, F. W. Van Keuls, C. H. Mueller, R. E. Treece, and T. V. Rivkin, Integr. Ferroelectr. **17**, 231 (1997).
[4] D. C. DeGoot, J. A. Beall, R. B. Marks, and D. A. Rudman, IEEE Trans. Appl. Supercond. **5**, 2272 (1995).
[5] R. J. Cava, J. Mater. Chem. **11**, 54 (2001).
[6] X. H. Zhu, S. G. Lu, C. L. Choy, H. L. W. Chan, and K. H. Wong, Integr. Ferroelectr. **36**, 73 (2001).
[7] S. S. Gevorgian, T. Martinsson, P. L. J. Linner, and E. L. Kollberg, IEEE Trans. Microwave Theory Tech. **44**, 896 (1996).
[8] V. M. Mukhortov, Y. S. Nikitin, M. G. Rdchenko, V. A. Aleshin, Y. I. Golovko, and V. P. Dudkevich, Sov. Phys. Tech. Phys. **31**, 805 (1986).
[9] Z. Surowiak, E. Nogas, A. M. Margolin, I. N. Zakharchenko, and S. V. Biryukov, Ferroelectrics **115**, 21 (1991).
[10] J. Chen, L. A. Wills, B. W. Wessels, D. L. Schultz, and T. J. Marks, J. Electron. Mater. **22**, 701 (1993).
[11] S. Bilodeau, R. Carl, and P. C. Van Buskirk, Mater. Res. Soc. Symp. Proc. **415**, 219 (1996).
[12] B. H. Hoerman, G. M. Ford, L. D. Kaufman, and B. W. Wessels, Appl. Phys. Lett. **73**, 2248 (1998).
[13] C. M. Carlson, T. V. Rivkin, P. A. Parilla, J. D. Perkins, D. S. Ginley, A. B. Kozyrev, V. N. Oshadchy, and A. S. Pavlov, Appl. Phys. Lett. **76**, 1920 (2000).
[14] M. P. McNeal, S. J. Jang, and R. E. Newnham, J. Appl. Phys. **83**, 3288 (1998).
[15] M. S. Tsai, S. C. Sun, and T. Y. Tseng, J. Appl. Phys. **82**, 3482 (1997).