Microwave properties of epitaxial (111)-oriented $Ba_{0.6}Sr_{0.4}TiO_3$ thin films on $Al_2O_3(0001)$ up to 40 GHz

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Perovskite $Ba_{0.6}Sr_{0.4}TiO_3$ (BST) thin films have been grown on $Al_2O_3(0001)$ substrates without/with inserting an ultrathin TiO_x seeding layer by rf magnetron sputtering. X-ray diffraction and pole figure studies reveal that the film with the TiO_x layer (12-Å-thick) is highly oriented along the (111) direction and exhibits a good in-plane relationship of BST(111)$\|$$Al_2O_3(0001)$. The high frequency dielectric measurements demonstrate that the complex permittivity ($\varepsilon=\varepsilon'-j\varepsilon''$) is well described by a Curie–von Scheidler dispersion with an exponent of 0.40. The resulting epitaxial BST films show high permittivity (~428) and tunability (~41%, at 300 kV/cm and 40 GHz) and their microwave properties (1–40 GHz) potentially could be made suitable for tunable devices. © *2010 American Institute of Physics*. [doi:10.1063/1.3478015]

$Ba_{1-x}Sr_xTiO_3$(BST) is a material with enormous potential for the application in capacitors of dynamic random access memories,[1,2] tunable microwave ,[3–5] and power-supply decoupling[6] because of its high permittivity and relatively low dielectric loss. The application as tunable devices for telecommunications which are operated in the microwave range (300 MHz to 300 GHz) requires detailed knowledge of the microwave properties in the high-frequency domain.[7,8] Although ferroelectric materials in thin-film form often show inferior properties as compared to bulk ceramics, it has been demonstrated that high quality epitaxial films generally have much better properties than polycrystalline films.[9–11]

Very recently, it was shown that by depositing epitaxial (111)-oriented BST films on $Al_2O_3(0001)$ substrates, it is possible to obtain higher tunability while keeping the microwave loss low compared to polycrystalline BST films.[12] Xiao *et al.*[13] also reported that epitaxial (001)-oriented BST films on $MgO/ZnO/Al_2O_3(11\bar{2}0)$ substrates revealed a very high dielectric tunability of up to 84% at 1 MHz in 5 μm gap interdigital capacitor. All the above recent advancements have certainly paved the way for the realization of high frequency microwave applications based on the epitaxial-BST thin film capacitors. Here, we present our recent achievements of the microwave dielectric properties of the highly epitaxial as well as polycrystalline BST films on $Al_2O_3(0001)$ over a wide range of microwave frequencies (1–40 GHz), rather than at the lower, narrower frequency ranges ($\leq$10 GHz) more commonly studied.[8]

An ultrathin TiO_x layer with thickness ~12 Å was first deposited on $Al_2O_3(0001)$ substrates by dc magnetron reactive sputtering at room temperature 450-nm-thick BST (x =0.4) films were then *in situ* (800 °C) deposited on Al_2O_3 and TiO_x-buffered/Al_2O_3 substrates by radio frequency magnetron sputtering from a stoichiometric $Ba_{0.6}Sr_{0.4}TiO_3$ ceramic target with excess BaO and SrO using an Ar/O_2 flow ratio of 70/30 sputtering gas mixture with total pressure of 15 mTorr and a sputter power of 70 W.[14] The deposition rate for both BST films under such conditions was about 1.64 nm/min. The structure properties, crystallinity and epitaxial behavior of BST films were characterized by an x-ray diffraction (XRD) with CuK_α radiation using $\theta-2\theta$ scan and pole figure. For microwave properties, coplanar waveguide (CPW) transmission lines (illustrated in Fig. 1) were defined by standard UV photolithographic lift-off technique using electron-beam evaporated Au/Ti (300-nm-thick) electrodes on both bare Al_2O_3 substrate and BST film surface. The microwave dielectric properties of BST films were measured as a function of frequency (1–40 GHz) and dc bias [(−30)–(30) V] by using a ground-signal-ground microprobe (Cascade Microtech) station connected to a vector network analyzer (Agilent Technologies E8361A). First, the complex propagation constant γ ($\gamma=\alpha+j\beta$) was calculated from the scattering parameters obtained from the microwave measurement. Second, the complex dielectric permittivity ε ($\varepsilon=\varepsilon'-j\varepsilon''$) of the substrate and conductor losses were extracted by fitting the experimental γ using a two-dimensional tangential vector finite element method coupled with software ELFI. Finally, the intrinsic ε of BST thin films was obtained by applying the same procedure. Further details were given elsewhere.[15,16]

Figure 2(a) shows the XRD $\theta-2\theta$ patterns of BST films grown on $Al_2O_3(0001)$ covered without/with TiO_x layer (12-Å-thick). The film directly grown on Al_2O_3 shows a dis-

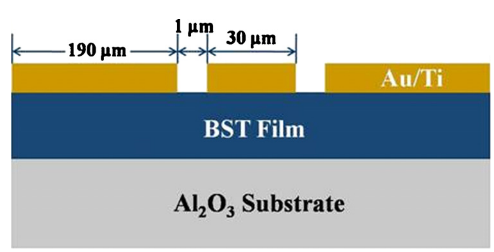

FIG. 1. (Color online) Cross-section view of CPW transmission lines structures. The length of CPW is 3 mm.

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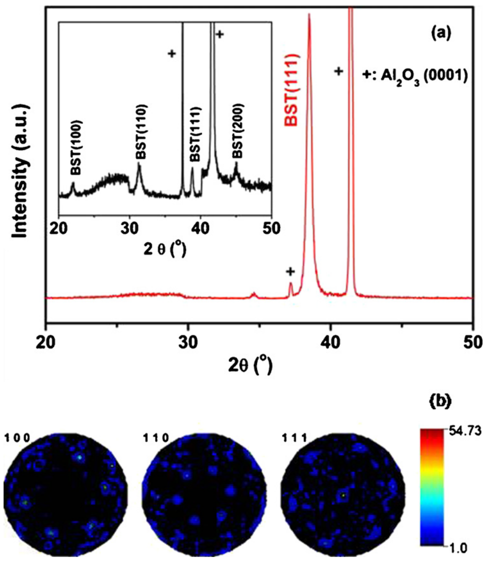

FIG. 2. (Color online) (a) XRD $\theta-2\theta$ patterns of the 450-nm-thick BST films on $Al_2O_3(0001)$ with 12-Å-thick TiO_x layer and (b) {100}, {110}, and {111} pole figures of BST thin films on $TiO_x/Al_2O_3(0001)$. The inset of (a) shows the XRD $\theta-2\theta$ patterns of the 470-nm-thick BST films on $Al_2O_3(0001)$ without TiO_x layer.

tinctly polycrystalline nature, while the film on TiO_x-covered Al_2O_3 surface shows a completely different growth behavior. Only one strong (111) peak without any peaks originating from other orientations can be found. The lattice parameters, for BST films are 4.026 Å (polycrystalline) and 4.045 Å (epitaxial), respectively, and the both are expanded compare to the bulk $Ba_{0.6}Sr_{0.4}TiO_3$. From these values, the misfit strain of the polycrystalline and epitaxial BST films is determined to be 1.54% and 2.01%, respectively. The lattice expansion of the BST films is a result of stresses caused by lattice mismatch, film-substrate thermal coefficient differences and oxygen vacancies.[17] The additional expansion for epitaxial BST could be ascribed to the larger misfit strains. The sixfold symmetry reflections from the {100}, {110}, and {111} poles can be clearly seen in the Fig. 2(b). Following the conclusion of Yamada *et al.*,[12] this sixfold symmetry corresponds to two in-plane variants of the threefold (111) orientation. The in-plane orientation relationship has been determined to be $BST(111)\|Al_2O_3(0001)$.

Figures 3(a) and 3(b) show real (ε') and imaginary part of permittivity (ε'') of BST films grown on Al_2O_3 covered without/with TiO_x layer as a function of frequency. It is found that ε' of both BST thin films slightly decreased over the measured frequency range, and the enhanced dielectric properties for the BST(111) film are observed in the measured frequency range. The large observed ε' can be attributed to largely (111)-oriented domain structure and the high crystallinity of the film. On the other hand, a power-law dispersion of ε' and ε'' is noted. The empirical dispersion is given by the Curie-von Schweidler relationship as follows:[18]

$$\varepsilon'_{(\omega)} = \varepsilon'_{(0)} - A'\omega^m,$$

$$\varepsilon''_{(\omega)} = A'\omega^m.$$

In these expressions, ω and $\varepsilon'_{(0)}$ are the angular frequency and the static dielectric constant, respectively, and A', A'', and m are constants. The fitting curve in Fig. 3 is

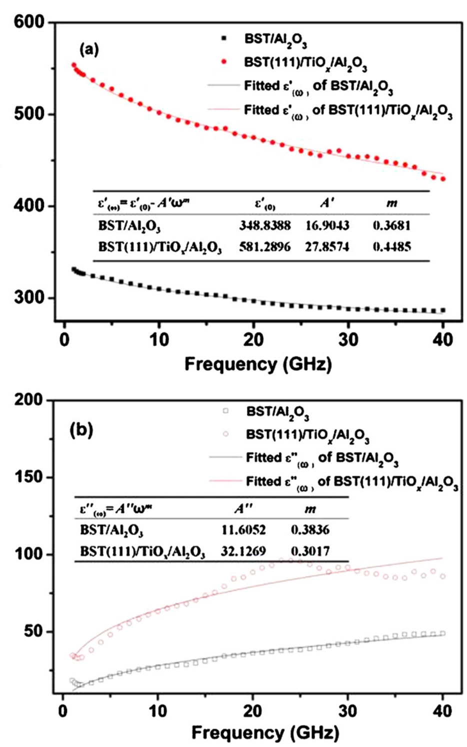

FIG. 3. (Color online) Frequency spectrum of (a) real part of permittivity (ε') and (b) imaginary part of permittivity (ε'') for BST thin films grown on $Al_2O_3(0001)$ covered without/with 12-Å-thick TiO_x layer. Data follow a Curie-von Schweidler power law.

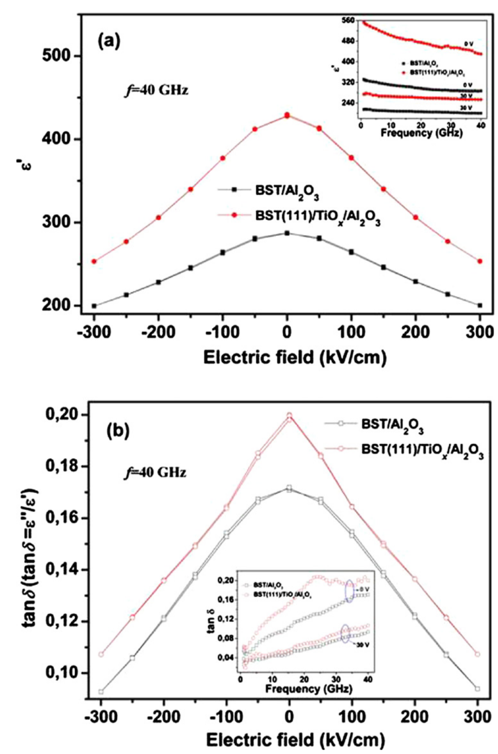

FIG. 4. (Color online) The electric field dependence of (a) ε' and (b) loss tangent ($\tan\delta=\varepsilon''/\varepsilon'$) of BST thin films deposited on with and without the insertion of the TiO_x buffer layer at 40 GHz, respectively. Inset of (a) ε' and (b) $\tan\delta$ (0–30 V) for BST films as a function of frequency.

TABLE I. Microwave dielectric properties for both epitaxial and polycrystalline BST films. The zero-bias permittivity and loss tangent, tunability at 300 kV/cm, FOM, and CQF at 1, 10, and 40 GHz are given. (The formula for calculating the CQF and FOM is taken from Ref. 22 and Ref. 26, respectively.)

	Frequency (GHz)	ε' at 0 V	Tunability at 30 V(%)	tan δ at 0 V	FOM	CQF
BST(111)/TiO_x/Al_2O_3	1	554	50.5	0.063	801.5	309.1
BST/Al_2O_3		331	35.14	0.056	632.24	95.7
BST(111)/TiO_x/Al_2O_3	10	502	47.1	0.126	373.6	69.15
BST/Al_2O_3		310	32.63	0.088	371.51	40.65
BST(111)/TiO_x/Al_2O_3	40	430	41.1	0.2	204.9	13.3
BST/Al_2O_3		287	30.16	0.17	176.56	8.12

calculated by fitting the complex permittivity of the dispersion curve to obtain $\varepsilon'_{(0)}$, A', A'', and m which are listed inset of Figs. 3(a) and 3(b). Values for the exponent m are in the range of 0.3–0.5, which is comparable to the values reported for the frequency range of 1 mHz to 20 GHz.[19] Our fitting curves provided $\varepsilon'_{(0)}$ of 581 and 349 for BST(111)/TiO_x/Al_2O_3 and BST/TiO_x/Al_2O_3, respectively. The Curie-von Schweidler behavior is in consistent with observations in epitaxial and polycrystalline $BaTiO_3$, and has been reported to persist up to gigahertz range.[20]

Microwave properties of both epitaxial and polycrystalline BST films on Al_2O_3 up to 40 GHz are presented in Fig. 4 and compiled in Table I. The tunability, defined as $\{(\varepsilon'(0) - \varepsilon'(V_{max})/\varepsilon'(0)\} \times 100\%$, where $\varepsilon'(0)$, $\varepsilon'(V_{max})$ are the ε' of BST film at zero and the maximum applied voltage, respectively. A prominent enhancement tunability of 41% can be achieved for the BST(111)/TiO_x/Al_2O_3 film, as compared to 30% obtained with BST/Al_2O_3 film, at 40 GHz and 300 kV/cm. For an epitaxial (111)-oriented $Ba_{0.3}Sr_{0.7}TiO_3$ film and polycrystalline $Ba_{0.5}Sr_{0.5}TiO_3$ film on sapphire, the tunability was 33.87% (8 GHz, 200 kV/cm) (Ref. 12) and 26% (20 GHz, 200 kV/cm),[21] respectively. At zero-bias voltage, the tan δ at 1 GHz for BST/Al_2O_3 and BST(111)/TiO_x/Al_2O_3 film is 0.063 and 0.056, respectively, versus 0.045 as reported by Razumov *et al.*[22] While both presently obtained BST films have high losses (0.088–0.126 at 10 GHz and 0.17–0.2 at 40 GHz), larger than that of 0.04 in $Ba_{0.5}Sr_{0.5}TiO_3$ obtained by postdeposition anneal at 900 °C (Ref. 23) and 0.07 in $Ba_{0.3}Sr_{0.7}TiO_3$ film,[16] respectively. The presently obtained BST films to have so high losses could be ascribed to different (Ba+Sr)/Ti ratios, deposition conditions, lack of postannealing, and too high deposition temperature.[22,23] Other factors such as oxygen nonstoichiometry and sputtering pressure range could also be considered.[17] Moreover, the loss for epitaxial BST film is higher than that of polycrystalline film, which could be caused by larger misfit strain in the epitaxial film. The loss at high frequencies is significantly larger than the loss at 1 MHz (0.015).[24] The increase in tan δ in the microwave frequency range can be thought of to be due to a number of reasons, both of intrinsic and of extrinsic nature.[25] The figure of merit (FOM) (Ref. 26) and Communication quality factor (CQF) (Ref. 22) are also calculated and listed in Table I. The epitaxial BST(111) film grown on TiO_x/Al_2O_3 substrate had a larger FOM value (801.5) and CQF (309.1) at 1 GHz as a result of the improved tuning capability. In comparison, a CQF of 16000 at 1 GHz was reported in Ref. 22. Overall, the epitaxial BST films show superior microwave properties for the development of high frequency tunable microwave elements operating at room temperature.

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[1] D. E. Kotecki, Integr. Ferroelectr. **16**, 1 (1997).
[2] C. S. Hwang, S. O. Park, H.-J. Cho, C. S. Kang, H. K. Kang, S. I. Lee, and M. Y. Lee, Appl. Phys. Lett. **67**, 2819 (1995).
[3] J. Im, O. Auciello, and S. K. Streiffer, Thin Solid Films **413**, 243 (2002).
[4] D. Dimos and C. H. Mueller, Annu. Rev. Mater. Sci. **28**, 397 (1998).
[5] M. W. Cole, P. C. Joshi, M. Ervin, M. Wood, and R. L. Pfeffer, J. Appl. Phys. **92**, 3967 (2002).
[6] D. S. Jeong, C. S. Hwang, J. D. Baniecki, T. Shioga, K. Kurihara, N. Kamehara, and M. Ishii, Appl. Phys. Lett. **87**, 232903 (2005).
[7] I. P. Koutsaroff, T. A. Bernacki, M. Zelner, A. Cervin-Lawry, T. Jimbo, and K. Suu, Jpn. J. Appl. Phys., Part 1 **43**, 6740 (2004).
[8] M. W. Cole, C. V. Weiss, E. Ngo, S. Hirsch, L. A. Coryell, and S. P. Alpay, Appl. Phys. Lett. **92**, 182906 (2008).
[9] S. W. Liu, Y. Lin, J. Weaver, W. Donner, X. Chen, C. L. Chen, J. C. Jiang, E. I. Meletis, and A. Bhalla, Appl. Phys. Lett. **85**, 3202 (2004).
[10] T. Yamada, K. F. Astafiev, V. O. Sherman, A. K. Tagantsev, P. Muralt, and N. Setter, Appl. Phys. Lett. **86**, 142904 (2005).
[11] W. Chang, S. W. Kirchoefer, J. M. Pond, J. S. Horwitz, and L. Sengupta, J. Appl. Phys. **92**, 1528 (2002).
[12] T. Yamada, P. Muralt, V. O. Sherman, C. S. Sandu, and N. Setter, Appl. Phys. Lett. **90**, 142911 (2007).
[13] B. Xiao, H. R. Liu, V. Avrutin, J. H. Leach, E. Rowe, H. Y. Liu, Ü. Özgür, H. Morkoç, W. Chang, L. M. B. Alldredge, S. W. Kirchoefer, and J. M. Pond, Appl. Phys. Lett. **95**, 212901 (2009).
[14] L. H. Yang, G. S. Wang, D. Rémiens, and X. L. Dong, J. Am. Ceram. Soc. **93**, 2526 (2010).
[15] F. Ponchel, J.-F. Legier, C. Soyer, D. Rémiens, J. Midy, T. Lasri, and G. Guéguan, Appl. Phys. Lett. **96**, 252906 (2010).
[16] F. Ponchel, J. Midy, J. F. Legier, C. Soyer, D. Rémiens, T. Lasri, and G. Guéguan, J. Appl. Phys. **107**, 054112 (2010).
[17] A. L. Campbell, R. R. Biggers, G. Subramanyam, G. Kozlowski, R. A. Kleismit, H. N. Zate, S. C. Hopkins, B. A. Glowacki, B. D. Riehl, and T. L. Peterson, Nanotechnology **19**, 485704 (2008).
[18] B. H. Hoerman, G. M. Ford, L. D. Kaufmann, and B. W. Wessels, Appl. Phys. Lett. **73**, 2248 (1998).
[19] J. D. Baniecki, R. B. Laibowitz, T. M. Shaw, P. R. Duncombe, D. A. Neumayer, D. E. Kotecki, H. Shen, and Q. Y. Ma, Appl. Phys. Lett. **72**, 498 (1998).
[20] T. Hamano, D. J. Towner, and B. W. Wessels, Appl. Phys. Lett. **83**, 5274 (2003).
[21] J.-Y. Kim and A. M. Grishin, Appl. Phys. Lett. **88**, 192905 (2006).
[22] S. V. Razumov, A. V. Tumarkin, M. M. Gaidukov, A. G. Gagarin, A. B. Kozyrev, O. G. Vendik, A. V. Ivanov, O. U. Buslov, V. N. Keys, L. C. Sengupta, and X. Zhang, Appl. Phys. Lett. **81**, 1675 (2002).
[23] E. A. Fardin, A. S. Holland, K. Ghorbani, and P. Reichart, Appl. Phys. Lett. **89**, 022901 (2006).
[24] Y. Wang, B. T. Liu, Z. M. Yang, and J. Du, Appl. Phys. Lett. **90**, 042905 (2007).
[25] A. K. Tagantsev, V. O. Sherman, K. F. Astafiev, J. Venkatesh, and N. Setter, J. Electroceram. **11**, 5 (2003).
[26] H. S. Kim, T. S. Hyun, H. G. Kim, I. D. Kim, T. S. Yun, and J. C. Lee, Appl. Phys. Lett. **89**, 052902 (2006).