$Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$/Mn-doped $Ba_{0.6}Sr_{0.4}TiO_3$ heterolayered thin films with enhanced tunable performance

Wangyang Fu,[1] Hong Wang,[2] Lingzhu Cao,[3] and Yueliang Zhou[1,a)]
[1]*Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China*
[2]*Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China*
[3]*College of Materials Science and Engineering, Beijing University of Technology, Beijing 100022, People's Republic of China*

(Received 9 March 2008; accepted 14 April 2008; published online 9 May 2008)

$Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$/Mn-doped $Ba_{0.6}Sr_{0.4}TiO_3$ heterolayered thin films were deliberately deposited on Pt/Ti/SiO_2/Si substrate by pulsed laser deposition and used as tunable materials. The heterolayered films exhibit prominently enhanced tunable performance compared to previous reported dielectric/ferroelectric layered composite films, i.e., a repeatable large tunability of 55%–60% measured under dc bias field of 570 kV/cm, with temperature insensitive permittivity near room temperature, while the dielectric losses can be safely maintained below 0.5%. The results indicate that $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$/Mn-doped $Ba_{0.6}Sr_{0.4}TiO_3$ heterolayered thin films are excellent candidates for electrically steerable applications. © *2008 American Institute of Physics*.
[DOI: 10.1063/1.2924278]

The progress on miniaturization and integration of the microwave devices strongly depends on the ability to fabricate high quality tunable thin films possessing both high tunability and low losses.[1,2] For these applications, ferroelectric $Ba_xSr_{1-x}TiO_3$ (BST),[3–6] currently being most widely studied for room-temperature integration into microwave devices such as phase shifters, tunable filters, and steerable antennas, seems to be the material of choice. However, its high dielectric loss (generally $>10^{-2}$) is a crucial limitation for practical utilizations.[7–9] In order to reduce the dielectric loss of pure BST materials, great efforts have been made in the past decades. Among various approaches, dielectric/ferroelectric layered composite was proved to be a flexible and efficient way.[1,2,10–13] Nonetheless, the dielectric layer with low permittivity inclines to consume a majority of bias voltage, resulting in a deteriorated tunable performance of the composite.

Very recently, researches on BST-$Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ (BZN) based composite structure have started up.[14–17] Compared to other low-loss dielectrics (with low permittivity, MgO ~ 8, SiO_2 ~ 4, etc.), BZN (Refs. 18–24) offers much higher permittivity (~200) with additional tunability, thus sharpening the overall dielectric tunable performance as a whole. However, even for BST-BZN based composite films, the maximum normal tunability at room temperature reported up to now is only about 25%,[16] which cannot be competitive with that of up to 55% for BZN or even more for BST material. So, it is really desirable to prepare highly tunable, low losses composite films, before any tunable applications of BST-BZN based composite films can be fulfilled.

In this letter, we show that even higher tunability (60%) and lower loss tangent can be achieved in deliberately deposited BZN/Mn–BST heterolayered films. A temperature insensitive permittivity of the heterolayered films near room temperature is also reported.

For pulsed laser deposition (PLD) experiment, conventional ceramic processing was used to prepare the BZN and 2% additional Mn-doped $Ba_{0.6}Sr_{0.4}TiO_3$ ceramic disk-type targets (Mn acceptor doping is well known[2,11] as an efficient way to improve the crystallization and dielectric performances of BST thin films). As for deposition, a 308 nm XeCl excimer laser with laser energy density of 2 J/cm^2 was used to ablate the ceramic targets. An initial 300 nm thick highly crystal Mn–BST layer was deposited on Pt/Ti/SiO_2/Si substrate at 800 °C with 10 Pa oxygen pressure, followed by an additional growth of a 50 nm thin BZN film at a reduced substrate temperature of 650 °C to prevent any phases except cubic pyrochlore from forming and also alleviate possible interdiffusion between the Mn-BST and BZN component layers. The schematic of the device structure (a paralleled capacitance) for dielectric characterization is illustrated in the inset of Fig. 2. Au top electrodes with low electrical resistivity were applied.[24] Phase composition and crystallization of the Mn–BST (gray solid line) and the heterolayered films (black solid line) deposited on Pt/Ti/SiO_2/Si substrate were characterized by x-ray diffraction (XRD). As shown by the black solid line in Fig. 1, the peaks located at 39.8°and 38.4°indicate the (111) textured of both Pt bottom electrode and Au top electrode, which were deposited by PLD without intentional heating. The heterolayered films have a well defined crystalline structure. Besides the intense (111) diffraction peak around 39° originated from the perovskite Mn-BST, the sharp BZN diffraction peaks show no obvious texture as compared to those of BZN powder in cubic pyrochlore phase, revealing the polycrystalline nature of the BZN film deposited on (111) oriented Mn-BST film. No other phases and no noticeable changes in the lattice parameter of Mn-BST can be detected with BZN dielectric inclusion, which excludes interdiffusion between the two layers during deposition. Dielectric measurements were

a)Author to whom correspondence should be addressed. Electronic mail: ylzhou@aphy.iphy.ac.cn.

 © 2008 American Institute of Physics
Downloaded 10 Dec 2008 to 159.226.36.218. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp

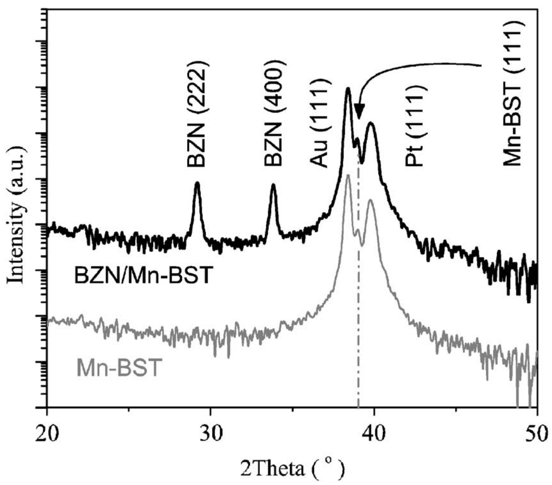

FIG. 1. XRD patterns of Mn BST and BZN/Mn–BST heterolayered thin films deposited on $Pt/Ti/SiO_2/Si$ substrate with Au top electrodes.

taken using 500 mV oscillation voltage by an Agilent 4294A precise impendence analyzer at room temperature, if without declaration.

Figure 2 shows the frequency dependent permittivity and loss tangent of the heterolayered films measured without dc bias field. It is observed that although the permittivity of the heterolayered films exhibits a frequency independent characteristic, the loss tangent increases with the increasing frequency after 100 kHz, which should be attributed to the conductor loss contribution of the electrodes as debated by Lu and Stemmer.[20]

The bias field dependent permittivity of the heterolayered films was measured. It turns out that a large tunability of 55%–60% can be achieved in a repeatable manner. As an example, Fig. 3 shows the bias field dependent permittivity and loss tangent of the heterolayered films measured at 100 kHz, from which a large dielectric tunability of 60% under an applied bias field of +570 kV/cm can be seen. Here, we defined the relatively tunability n_r as $\{[\varepsilon(0)-\varepsilon(E_{\max})]/\varepsilon(0)\}\times 100\%$, where $\varepsilon(0)$ is the maximum permittivity at zero bias and $\varepsilon(E_{\max})$ the minimum permittivity at the maximum applied field. Such a high tunability is in good agreement with our previous simulation,[16] in which careful calculation suggested that a tunability of ~40% might be achieved under a bias field of 420 kV/cm, when a thin BZN layer of 50 nm is adopted in the BZN/Mn–BST

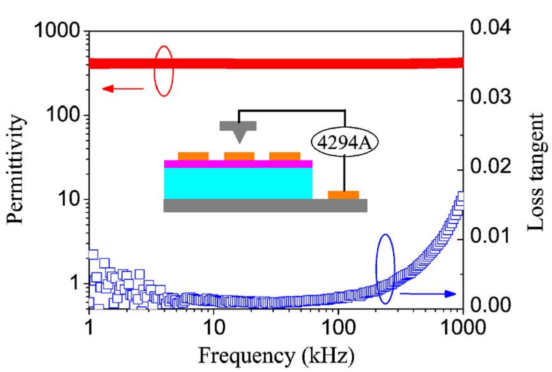

FIG. 2. (Color online) Permittivity and loss tangent as a function of frequency for BZN/Mn–BST heterolayered thin films, measured without dc bias field. Inset is the scheme of the device structure (a paralleled capcitance) for dielectric characterization.

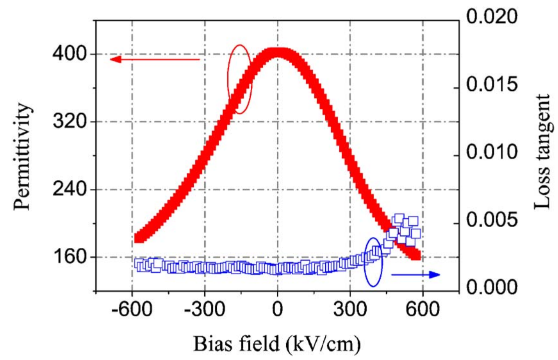

FIG. 3. (Color online) Bias field dependent permittivity and loss tangent of the BZN/Mn–BST heterolayered thin films measured at 100 kHz. The tunability is figured out as 60% at +570 kV/cm and the loss tangent is below 0.005, giving a FOM of 120.

heterolayered films with a total thickness of 450 nm. Higher bias field would lead to more tunability. If defined as the thickness, SiO_2 would have to be in order to have the same capacitance per unit area. The effective oxide thickness (EOT) of the BZN layer in previous reported BST-BZN composite films[15,16] can be figured out as 4–5 nm, which consumes a great part of the bias voltage and is responsible for the deteriorated tunability. Here, a 50 nm thin BZN layer with EOT as small as 1 nm ensures a much reduced consumption of the bias voltage and is easy to be handled in practice, thus defend a large tunability of the composite in a repeatable manner.

It is believed[1] that dielectric/ferroelectric composite films with well defined layered structure should behave just like a ferroelectric film but with lower Curie–Weiss temperature. Here, we instructively use the expression for the field E needed to achieve a given tunability n_r,

$$E = \frac{\sqrt{n_r}(3-2n_r)}{\varepsilon_0\sqrt{27\beta\varepsilon_0(1-n_r)^3}}\frac{1}{\varepsilon(0)^{3/2}}. \qquad (1)$$

The results are summarized in Table I. The coefficient of the dielectric nonlinearity β of the heterolayered films can be calculated as $7.8\times10^9\ J/C^4\,m^5$. As a comparison, the β value of the heterolayered films is much larger than that $(9.7\times10^8\ J/C^4\,m^5)$ of previous reported BZN/BST/BZN sandwich films and close to that $(8\times10^9\ J/C^4\,m^5)$ typically of $SrTiO_3$, revealing the high crystallization of the Mn–BST layer in the heterolayered films. The limited β of the sandwich films is due to an insufficient crystallization of the perovskite BST component deposited under a compromised temperature in order to stabilize BZN in cubic phase and prevent interdiffusion from happening, as mentioned by the authors.[15]

As shown in Fig. 3, the loss tangent of the heterolayered films is below 0.002 at zero bias field and increases to 0.005 at the maximum field of +570 kV/cm. It is documented that higher leakage current originated from the imperfect insulator properties of the tunable films would result in higher dielectric loss at low frequency.[20] Based on this model, we measured the bias field dependent leakage current of the heterolayered films. Consequently, the conductive loss contribution at high positive bias field can be calculated out as $\sim10^{-3}$, which is in satisfactory agreement with the experimental observation. Actually, by depositing thicker BZN layer up to 100 nm to restrict leakage current at high bias

Downloaded 10 Dec 2008 to 159.226.36.218. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp

TABLE I. A comparison of the tunable characteristics of the heterolayered thin films with those of BZN/BST/BZN sandwich films.

	n_r	tan δ	$\varepsilon(0)$	E (kV/cm)	β (J/C^4 m^5)
BZN/Mn-BST	60%	<0.5%	400	570	7.8×10^9
BZN/BST/BZN[a]	11%	~0.8%	224	770	9.7×10^8

[a]Reference 15.

field, dielectric loss below 0.001 can be achieved in the whole measurement range, at the cost of a reduced tunability (~20%). Generally, the loss performance of the heterolayered films reported here is superior to or comparable to that of the state-of-art BST (around 0.005) and dielectric/ferroelectric layered composite films (10^{-3}).

In tunable microwave devices, the figure of merit (FOM) is used to evaluate the quality of the films, which is the optimum combination of high tunability and low dielectric loss: $n_r/\tan\delta$. Thereby, we obtained a FOM of 120, which is much better than that of previously reported BST–BZN based composite films,[14–17] and among one of the best results[6,22] of tunable materials achieved up to now.

The asymmetry characteristics of the bias field dependent permittivity (as well as the loss tangent) of the heterolayered films should be mentioned. Similar asymmetry has not been observed in BZN single layer films or BST/BZN/BST sandwich films with symmetry structures,[20,21,15] which suggests that the asymmetry configuration of the BZN/Mn–BST heterolayered films should be responsible for the observed asymmetry in both curves.

Last but not least, we measured the temperature dependent permittivity of the BZN/Mn–BST heterolayered thin films under 100 kHz, as shown in Fig. 4. Interestingly, the temperature coefficient of capacitance is −170 ppm/°C measured in the temperature from −60 to 60 °C, which is comparable to that of −185 and −230 ppm/°C for laser annealing and rapid thermal annealed BZN films, respectively.[21,23] The result is in consistence with the measured linear *P-E* curve (by a RT6000S Ferroelectric Test System), indicating that the heterolayered thin films is not ferroelectric near room temperature. Such temperature-stable characteristics would surely be beneficial to practical applications. Further works on the characterization of the microwave properties of the heterolayered films are under way.

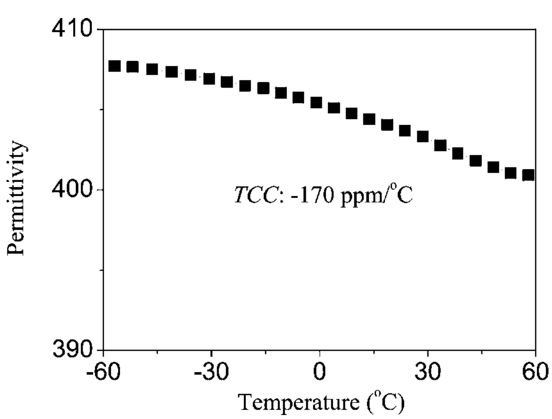

FIG. 4. Temperature dependent permittivity of BZN/Mn–BST heterolayered thin films under 100 kHz.

In summary, we have fabricated well crystallized BZN/Mn–BST heterolayered films with 50 nm thin BZN layer by PLD on $Pt/Ti/SiO_2/Si$ substrate. Compared to previously reported dielectric/ferroelectric layered composite films, the BZN/Mn–BST heterolayered thin films exhibited prominently enhanced tunable performances, i.e., significant improvements of the tunability (55%–60%) and dielectric loss (<0.5%) as a whole with a temperature-stable permittivity, which indicates an attractive prospect for microwave applications.

The authors are grateful for the financial support of the National Natural Science Foundation of China (60371032).

[1]A. K. Tagantsev, V. O. Sherman, K. F. Astafiev, J. Venkatesh, and N. Setter, J. Electroceram. **11**, 5 (2003).
[2]Z. Yuan, Y. Lin, J. Weaver, X. Chen, C. L. Chen, G. Subramanyam, J. C. Jiang, and E. I. Meletis, Appl. Phys. Lett. **87**, 152901 (2005).
[3]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).
[4]B. H. Park, E. J. Peterson, Q. X. Jia, J. Lee, X. Zeng, W. Si, and X. X. Xi, Appl. Phys. Lett. **78**, 533 (2001).
[5]S. S. Gevorgian and E. L. Kollberg, IEEE Trans. Microwave Theory Tech. **49**, 2117 (2001).
[6]A. Vorobiev, P. Rundqvist, K. Khamchane, and S. Gevorgian, Appl. Phys. Lett. **83**, 3144 (2003).
[7]B. L. Cheng, C. Wang, S. Y. Wang, T. W. Button, H. B. Lu, Y. L. Zhou, Z. H. Chen, and G. Z. Yang, Appl. Phys. Lett. **84**, 5431 (2004).
[8]N. Setter, D. Damjanovic, L. Eng, G. Fox, S. Gevorgian, S. Hong, A. Kingon, H. Kohlstedt, N. Y. Park, G. B. Stephenson, I. Stolitchnov, A. K. Taganstev, D. V. Taylor, T. Yamada, and S. Streiffer, J. Appl. Phys. **100**, 051606 (2006).
[9]J. F. Scott, Science **315**, 954 (2007).
[10]M. W. Cole, W. D. Nothwang, C. Hubbard, E. Ngo, and M. Ervin, J. Appl. Phys. **93**, 9218 (2003).
[11]X. H. Zhu, D. N. Zheng, W. Peng, J. Li, and Y. F. Chen, Mater. Lett. **60**, 1224 (2006).
[12]V. Reymond, D. Michau, S. Payan, and M. Maglione, Ceram. Int. **30**, 1085 (2004).
[13]V. O. Sherman, A. K. Tagantsev, and N. Setter, Appl. Phys. Lett. **90**, 162901 (2007).
[14]L. Yan, L. B. Kong, L. F. Chen, K. B. Chong, C. Y. Tan, and C. K. Ong, Appl. Phys. Lett. **85**, 3522 (2004).
[15]S. X. Wang, M. S. Guo, X. H. Sun, T. Liu, M. Y. Li, and X. Z. Zhao, Appl. Phys. Lett. **89**, 212907 (2006).
[16]W. Y. Fu, L. Z. Cao, S. F. Wang, Z. H. Sun, B. L. Cheng, Q. Wang, and H. Wang, Appl. Phys. Lett. **89**, 132908 (2006).
[17]P. Shi, W. Ren, X. Wu, R. Huang, L. Zhang, and X. Yao, Ferroelectrics **357**, 138 (2007).
[18]W. Ren, S. Trolier-McKinstry, C. A. Randall, and T. R. Shrout, J. Appl. Phys. **89**, 767 (2001).
[19]H. Wang, H. L. Du, and X. Yao, Mater. Sci. Eng., B **99**, 20 (2003).
[20]J. W. Lu and S. Stemmer, Appl. Phys. Lett. **83**, 2411 (2003).
[21]J. G. Cheng, J. L. Wang, T. Dechakupt, and S. Trolier-McKinstry, Appl. Phys. Lett. **87**, 232905 (2005).
[22]J. Park, J. W. Lu, S. Stemmer, and R. A. York, J. Appl. Phys. **97**, 084110 (2005).
[23]R. L. Thayer, C. A. Randall, and S. Trolier-McKinstry, J. Appl. Phys. **94**, 1941 (2003).
[24]J. W. Lu, S. Schmidt, D. S. Boesch, N. Pervez, R. A. York, and S. Stemmer, Appl. Phys. Lett. **88**, 112905 (2006).

Downloaded 10 Dec 2008 to 159.226.36.218. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp