Effect of $CaRuO_3$ interlayer on the dielectric properties of Ba(Zr,Ti)O_3 thin films prepared by pulsed laser deposition

X. G. Tang[a]
School of Physics and Optoelectric Engineering, Guangdong University of Technology, 729 East Dongfeng Road, Guangzhou 510090, People's Republic of China; Department of Applied Physics and Materials Research Centre, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

H. Y. Tian, J. Wang, K. H. Wong, and H. L. W. Chan
Department of Applied Physics and Materials Research Centre, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

(Received 17 January 2006; accepted 26 August 2006; published online 5 October 2006)

$Ba(Zr_{0.2}Ti_{0.8})O_3$ (BZT) thin films on $Pt(111)/Ti/SiO_2/Si(100)$ substrates without and with $CaRuO_3$ (CRO) buffer layer were fabricated at 650 °C *in situ* by pulsed laser deposition. The BZT thin films showed a dense morphology, many clusters are found on the surface images of BZT/Pt films, which are composed by nanosized grains of 25–35 nm; the average grain size of BZT/CRO films is about 80 nm, which lager than that of BZT/Pt thin film. The dielectric constants and dissipation factors of BZT/Pt and BZT/CRO thin films were 392 and 0.019 and 479 and 0.021 at 1 MHz, respectively. The dielectric constant of BZT/Pt and BZT/CRO thin films changes significantly with applied dc bias field and has high tunabilities and figures of merit of ~70% and 37 and 75% and 36, respectively, under an applied field of 400 kV/cm. The possible microstructural background responsible for the high dielectric constant and tunability was discussed. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2360177]

Barium strontium titanate (Ba,Sr)TiO_3 (BST) thin films have currently become very attractive for applications in decoupling capacitors, storage capacitors, dynamic random-access memory, and tunable microwave devices.[1,2] The large electric field-depended dielectric constant can be used for devices such as tunable oscillators, filters, and phase shifters. In such devices, it is desirable to have a high dielectric tunability in a certain electric field range and low dielectric loss. $Ba(Zr_yTi_{1-y})O_3$ (BZT) is a possible choice as an alternative to BST in the fabrication of ceramic capacitors[3,4] because Zr^{4+} is chemically more stable than Ti^{4+}. The ferroelectric phase transition at the Curie temperature (T_C) in BZT bulk ceramics is known to change significantly with Zr content. BZT ceramics exhibit a diffuse phase transition and have high tunability in compositions with $y \geqslant 0.20$.[3–6] The fabrication of BZT thin films by rf-magnetron sputtering,[7] sol-gel method,[8] and pulsed laser disposition (PLD),[9] and their dielectric properties have been reported recently. Many efforts have been made to improve the dielectric properties of the BST thin film capacitors, including using conductive oxide electrodes such as (Ba,Sr)RuO_3,[10] $(La_{0.7}Sr_{0.3})MnO_3$,[11] $LaNiO_3$,[12] and yttrium barrium copper oxide (YBCO).[13] The effects of $CaRuO_3$ buffer layer on the dielectric properties and tunability of BZT films have not yet been reported. In this work, $Ba(Zr_{0.2}Ti_{0.8})O_3$ thin films growth on $Pt/Ti/SiO_2/Si$ substrate without and with $CaRuO_3$ buffer layer were prepared by pulsed laser disposition. The orientation characteristics of grains, dielectric properties, tunability, and figure of merit of the columnar-grained $Ba(Zr_{0.2}Ti_{0.8})O_3$ thin films on $Pt/Ti/SiO_2/Si$ substrate without and with $CaRuO_3$ buffer layer are also reported.

$CaRuO_3$ (CRO) bottom electrode layer was grown on $Pt/Ti/SiO_2/Si$ substrates at 750 °C by rf-magnetron sputtering and using a CRO target. $Ba(Zr_{0.2}Ti_{0.8})O_3$ (BZT) thin films were grown on $Pt/Ti/SiO_2/Si$ and $CRO/Pt/Ti/SiO_2/Si$ substrates at 650 °C by pulsed laser deposition using a KrF eximer laser (Lambda Physik Complex) ($\lambda = 248$ nm, 650 mJ, 25 ns) and BZT target. Details of the deposition conditions are given in Table I. These BZT and CRO targets were prepared by sol-gel process[4] and conventional solid state reaction, respectively. These films were deposited at a laser repetition rate of 10 Hz and pulsed laser energy of 300 mJ. The base pressure of the system is 2 mTorr. The deposition rate was 25 nm/min and the deposition time is 25–30 min. The oxygen pressure was an important parameter and was kept at 200 mTorr. Finally, the thin films were crystallized *in situ* at 650 °C in 400 mTorr of oxygen for 20 min and cooled down slowly to room tem-

TABLE I. Deposition conditions of BZT thin films by PLD and CRO buffer layer by rf-magnetron sputtering.

Deposition parameter	$Ba(Zr_{0.2}Ti_{0.8})O_3$	$CaRuO_3$
Deposition method	PLD	Sputtering
Deposition temperature	650 °C	750 °C
Film thickness	600–800 nm	170 nm
Base vacuum	2×10^{-6} Torr	2×10^{-6} Torr
Energy (power) used	300 mJ/pulse	80 W
Repetition rate	10 Hz	⋯
Deposition time	30 min	120 min
Working pressure	200×10^{-6} Torr	200×10^{-6} Torr
O_2/Ar press ratio	10/0	8/2
Annealing temperature	650 °C	750 °C
Substrates	$CRO/Pt/Ti/SiO_2/Si$	$Pt/Ti/SiO_2/Si$

---

[a] Author to whom correspondence should be addressed; electronic mail: xgtang6@yahoo.com.

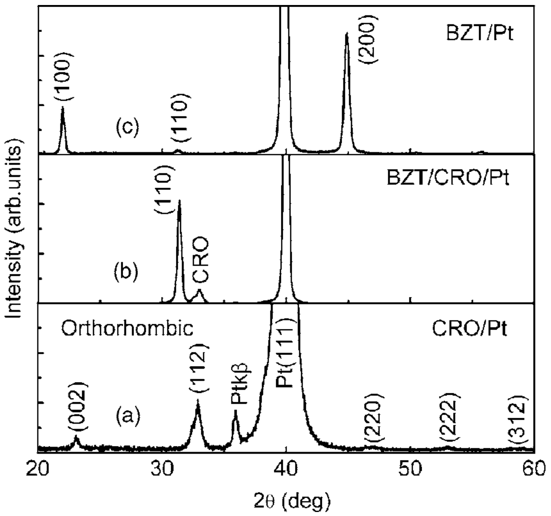

FIG. 1. XRD patterns of (a) CRO/Pt, (b) BZT/CRO/Pt, and (c) BZT/Pt.

perature and preferentially (100)- and (110)-oriented BZT films were fabricated.

The crystalline structure of the BZT thin films on Pt/Ti/SiO_2/Si substrate was analyzed using a Philips PW3710 x-ray diffractometer using Cu $K\alpha$ radiation with a Ni filter. Figure 1 shows the x-ray diffraction (XRD) pattern of the CRO and BZT thin films deposited on Pt/Ti/SiO_2/Si and CRO/Pt/Ti/SiO_2/Si substrates, respectively, and crystallized *in situ* at 650 °C for 20 min in oxygen atmosphere. CRO film grown on Pt/Ti/SiO_2/Si substrate has an orthorhombic phase structure [see Fig. 1(a)] and the relative peak intensity of (112) peak near 30° is the highest. BZT films deposited on Pt/Ti/SiO_2/Si substrates without and with CRO buffer layer have high (100)- and (110)-orientation [see Figs. 1(c) and 1(b)], respectively. The high (100)-orientation of BZT thin films is considered to be a self-textured growth in accordance with minimum surface energy conditions. On the other hand, a (110) plane is preferred in epitaxial textured growth and was observed in the present work whenever BZT thin layers were crystallized on CRO/Pt/Ti/SiO_2/Si substrates.

The thickness, surface, and cross-sectional morphologies of the thin films were determined by field emission scanning electron microscope (FE-SEM) (JEOL-JSM 6335F). Figure 2 shows the FE-SEM images of surface and cross sectional of the BZT thin films on Pt/Ti/SiO_2/Si substrates without and with CRO buffer layer. In Fig. 2, the thin films show homogenous and uniform microstructure. From Figs. 2(a) and 2(b), on the surface image of BZT/Pt thin films, many clusters are found, which are composed by nanosized grains of 25–30 nm. It is obvious that the cross-sectional image of BZT/Pt thin films has a columnar growth characteristic of the grains, and the grain sizes is about 25–30 nm. From Figs. 2(c) and 2(d), on the surface image of BZT/CRO thin films, the average grain size is about 80 nm. It is obvious that the cross-sectional image of BZT/CRO thin films has a columnar growth characteristic of the grains, and the grain sizes is about 30–50 nm. The grain size of BZT/CRO films is slightly larger than that of BZT/Pt film. From the FE-SEM images, it is seen that the BZT thin films is smooth and dense. The thicknesses of BZT/Pt and BZT/CRO thin films are 800 and 620 nm, respectively. The thicknesses of CRO and Pt electrodes are 170 and 110 nm, respectively.

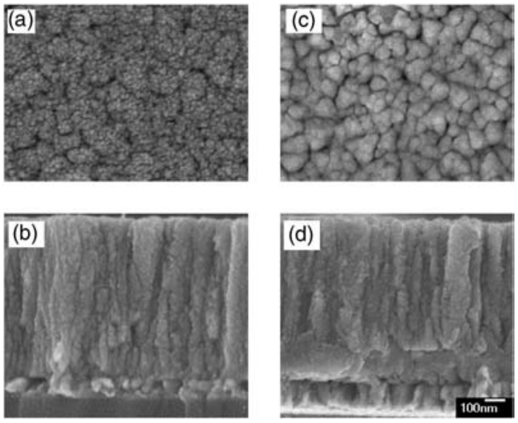

FIG. 2. FE-SEM photographs of BZT thin films deposited on [(a) and (b)] BZT/Pt and [(c) and (b)] BZT/CRO/Pt.

For electrical measurements of a thin film capacitor, top platinum (Pt) electrodes of 0.2 mm in diameter were deposited through a shadow mask onto the BZT thin films by pulsed laser deposition. The dielectric properties of Pt/BZT/Pt and Pt/BZT/CRO capacitors were measured using an Agilent 4294A impedance analyzers at room temperature. The dc bias field dependence of dielectric constant and dielectric loss at room temperature (300 K) were measured to evaluate the tunability of the BZT thin film. The measurements were conducted by applying a small ac signal of 0.5 V amplitude and 1 MHz frequency. The potential of the BZT films to be used in voltage-tunable devices depends on the ability to change the dielectric constant by means of an applied electric field. The electric field dependence of the dielectric constant and loss tan δ at room temperature is shown in Fig. 3 for the BZT/Pt and BZT/CRO thin films. As expected, a slim hysteresis was observed in BZT/Pt film as a result of the existence of ferroelectric domains at room temperature. In Fig. 3(b), at the first cycle, the permittivity is incomplete recovery. The value will decreases slightly after the first cycle, and then the value is stabilize. After first cycle, the sample shows similar saturation under unidirectional field application, and again is reproducible on subsequent cycling. The BZT films did not stable under long time application of such high fields. The breakdown field of BZT film is about 450 kV/cm. At zero electric field, the dielectric constant and loss tan δ are 392 and 0.019 and 479 and 0.021, respectively. A dielectric constant (ε) of 118 at 1 MHz was reported for sol-gel derived BZT (5/95) films on a Pt-coated Si substrate.[14] A series of ε values of 100, 150, and 250 at

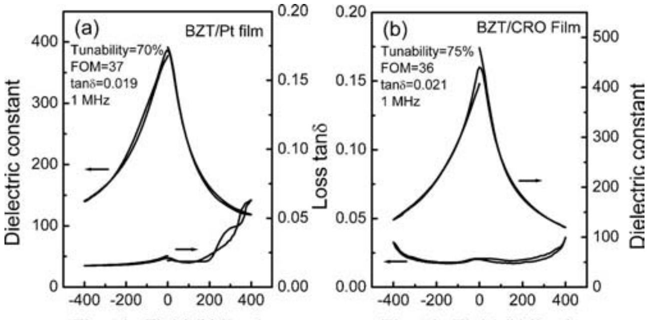

FIG. 3. Electric field dependence of the dielectric constant and loss tan δ of the Pt/BZT/Pt and Pt/BZT/CRO thin film capacitors at room temperature.

1 MHz has been reported for (111)-oriented BZT (20/80) films on Pt-coated Si substrates with various deposition temperatures prepared by sputtering.[7] A ε value of 452 at 100 kHz has been reported for BZT (10/90) thin film on Pt-coated Si substrate prepared by the PLD technique.[15]

The tunability is defined as $[\varepsilon_r(0)-\varepsilon_r(E)]/\varepsilon_r(0)$, where $\varepsilon_r(0)$ and $\varepsilon_r(E)$ are the dielectric constants measured at zero and a nonzero E field, respectively. The figure of merit (FOM) is defined as tunability/loss. The tunabilities and figures of merit (FOMs) are show in Fig. 3. From Fig. 3, the tunability is higher than 70% for the two films when applied an electric field of 400 kV/cm. The highest tunability of BZT/CRO films is up to 75%. The FOMs are 37 and 36, respectively, for BZT/Pt and BZT/CRO thin films. The value is higher than that of pulsed laser deposited random-oriented BZT(15/85) films (45% at 200 kV/cm),[9] higher than that of sol-gel derived BZT(35/65) films (38% at 600 kV/cm),[16] and the value is comparable with that of PLD deposited single BST layer thin films on (Ba,Sr)RuO_3 buffered Pt/Ti/SiO_2/Si substrate (70% tunability at 198 kV/cm)[10] and graded BST thin films on single crystal $LaAlO_3$ substrate with $(La_{0.7}Sr_{0.3})MnO_3$ bottom electrode (70% tunability at 450 kV/cm).[11] The $BaZr_{0.2}Ti_{0.8}O_3$ is near pinch off the three ferroelectric. The phase temperature near the room temperature and could easily be driven at high field levels. So, the film has high tunability. Padmini *et al.*[17] reported that when a BST film was subjected to tensile stress, a contraction occurred along the c axis leading to an enhancement of the in-plane oriented polar axis. By a converse electrostrictive effect, the in-plane tensile stress reduces the capacitance in the thickness direction of the film.[18] When higher voltages or electric fields were applied to the (100)-oriented BST thin films, the in-plane orientation of the polar axis resulted in higher tunability. Hence, the tunability of (100)-oriented BZT films was also has high value. On the other hand, interfaces between the ferroelectric thin films and the electrodes affect the measured dielectric properties. It has been proposed that the reduction of ε_r in ferroelectric thin films can be explained by the existence of interfacial "dead layer" at one or both metal electrodes with poor dielectric properties.[2,19–21] They may arise from the oxygen interdiffusion, chemical reaction, structural defects, or Schottky barriers at the interfaces. Treating the dead layer as a capacitance C_i in series with bulk film capacitance C_b, the measured capacitance may be expressed as $1/C=1/C_b+1/C_i$, and the dielectric constant of the dead layer increases as the film thickness decreases. Use the conductive oxide electrodes, such as (La,Sr)MnO_3, $CaRuO_3$, $LaNiO_3$, and YBCO, can decrease the thickness of the dead layer[22] and enhanced the dielectric constant and tunability.[2,10–12]

In conclusion, high (100)- and (110)-oriented columnar-grained BZT thin films deposited onto Pt/Ti/SiO_2/Si substrates without and with CRO buffer layer by pulsed laser deposition. At zero electric field, the dielectric constant and loss tan δ are 392 and 0.028 and 479 and 0.023, respectively. At room temperature and 1 MHz, the dependences of dielectric constant and tunability of the BZT/Pt and BZT/CRO thin films on the electric field were investigated, and the tunability and figure of merit are 70% and 37 and 75% and 36, respectively. The dielectric constant and tunability of the BZT thin films with high (110)-orientation were higher than that of the BZT thin film with (100)-orientation. Improved dielectric properties and tunability have been attributed to the (110) texture of the film, lager grain size, and CRO buffer layer. The BZT thin film is a promising candidate for tunable microwave device applications.

This work is supported by the Guangdong Provincial Natural Science Foundation of China (Grant No. 05001825), the Postdoctoral Fellowship Scheme, and the Centre for Smart Materials of the Hong Kong Polytechnic University.

[1] J. S. Scott, Annu. Rev. Mater. Sci. **28**, 79 (1998).
[2] X. X. Xi, H. C. Li, W. D. Si, A. A. Sirenko, I. A. Akimov, J. R. Fox, A. M. Clark, and J. H. Hao, J. Electroceram. **4**, 390 (2000).
[3] D. Hennings, A. Schnell, and G. Simon, J. Am. Ceram. Soc. **65**, 539 (1982).
[4] X. G. Tang, K. H. Chew, and H. L. W. Chan, Solid State Commun. **131**, 163 (2004).
[5] Z. Yu, C. Ang, R. Guo, and A. S. Bhalla, Appl. Phys. Lett. **81**, 1285 (2002).
[6] X. G. Tang, K. H. Chew, and H. L. W. Chan, Acta Mater. **52**, 5177 (2004).
[7] W. S. Choi, B. S. Jang, D. G. Lim, J. Yi, and B. Hong, J. Cryst. Growth **237-239**, 438 (2002).
[8] A. Dixit, S. B. Majumder, R. S. Katiyar, and A. S. Bhalla, Appl. Phys. Lett. **82**, 2679 (2003).
[9] A. R. James and C. Prakash, Appl. Phys. Lett. **84**, 1165 (2004).
[10] Y. A. Jeou, E. S. Choi, T. S. Seo, and S. G. Yoon, Appl. Phys. Lett. **79**, 1012 (2001).
[11] S. G. Lu, X. H. Zhu, C. L. Mak, K. H. Wong, H. L. W. Chan, and C. L. Choy, Appl. Phys. Lett. **82**, 2788 (2003).
[12] K. H. Yoon, J. H. Sohn, and B. D. Lee, Appl. Phys. Lett. **81**, 5012 (2002).
[13] D. Galt, J. C. Price, J. A. Beall, and R. H. Ono, Appl. Phys. Lett. **63**, 3078 (1993).
[14] X. G. Tang, H. L. W. Chan, and A. L. Ding, Thin Solid Films **460**, 227 (2004).
[15] S. Halder, S. Bhattacharyya, and S. B. Krupanidhi, Mater. Sci. Eng., B **95**, 124 (2002).
[16] J. Zhai, X. Yao, L. Zhang, and B. Shen, Appl. Phys. Lett. **84**, 3136 (2004).
[17] P. Padmini, T. R. Taylor, M. J. Lefevre, A. S. Nagra, R. A. York, and J. S. Speck, Appl. Phys. Lett. **75**, 3186 (1999).
[18] T. M. Shaw, Z. Suo, M. Huang, E. Liniger, R. B. Laibowitz, and J. D. Baniecki, Appl. Phys. Lett. **75**, 2129 (1999).
[19] C. Zhou and D. M. Newns, J. Appl. Phys. **82**, 3081 (1997).
[20] C. Basceri, S. K. Streiffer, A. I. Kingon, and R. Waser, J. Appl. Phys. **82**, 2497 (1997).
[21] C. Hofer, U. Ellerkamnn, S. Halder, R. Meyer, and R. Waser, J. Electroceram. **13**, 101 (2004).
[22] B. Chen, H. Yang, J. Miao, L. Zhao, L. X. Cao, B. Xu, X. G. Qiu, and B. R. Zhao, J. Appl. Phys. **97**, 024106 (2005).