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High tunability $(Ba,Sr)TiO_3$ thin films grown on atomic layer deposited TiO_2 and Ta_2O_5 buffer layers

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In this letter, we report on increased tunability of $Ba_{0.6}Sr_{0.4}TiO_3$ (BST) thin films by use of Ta_2O_5 and TiO_2 films as buffer layers between BST and Si substrates. Ta_2O_5 and TiO_2 buffer layers were grown by atomic layer deposition (ALD) onto Si substrates followed by pulsed laser deposition of $Ba_{0.6}Sr_{0.4}TiO_3$ thin films onto the buffer layers. The randomly oriented BST films deposited on TiO_2/Si substrates exhibited a broader grain size distribution than the (110) textured BST films grown on Ta_2O_5/Si substrates. At an applied voltage of 10 V, the BST films grown on Ta_2O_5/Si and TiO_2/Si substrates showed much enhanced tunability values of 53.1% and 72.9%, respectively, as compared to the 20.7% value obtained with BST films grown on MgO single crystal substrates. Successful integration of BST low voltage microwave tunable devices onto Si substrates thus appears possible with the aid of ALD grown Ta_2O_5 or TiO_2 buffer layers. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1821656]

The rapid worldwide growth of wireless communications, radar, and digital electronics has been a key driver in stimulating developments in the field of rf/microwave electronics with demands for ever higher frequencies, bandwidths, and data rates. Tunable high frequency devices are key components for the next generation of communications and radar systems.[1] Barium strontium titanate's (BST) capacitive properties can be tuned by more than 50% in metal–insulator–metal structures with low bias levels resulting in similar percentage changes in the frequency of tuned circuits.[2] Currently, BST-based tunable devices are typically fabricated on small area (1×1 in.^{2}) single crystal substrates such as $LaAlO_3$ and MgO providing good lattice match and low substrate dielectric loss. By replacing bulky hybrid tuned circuits with thin film elements directly integrated onto silicon chips, one reduces size and power consumption and promises improved reliability, reduced cost, and high volume production by use of large diameter Si wafers.[3] However, BST films grown directly onto Si suffer from low tunability due to the formation of low-K SiO_2 thin layers between BST and Si during the requisite high temperature BST deposition process. Furthermore, high microwave losses related to low resistivity Si have served as a barrier against the realization of BST and related device integration with Si microelectronics. To solve these problems, we introduce suitable oxide buffer layers (Ta_2O_5 and TiO_2) with high dielectric constants between the BST layers and the Si substrate. The buffer layers serve multiple purposes including electrical isolation, templates for high quality BST growth, stress control for crack-free films, and prevention of chemical reactions.[4,5] In order to obtain high quality buffer layers, we utilize atomic layer deposition (ALD), which is very suitable for forming very thin, smooth and conformal layers at low deposition temperatures.[6] Ta_2O_5 and TiO_2 thin films have been investigated for numerous integrated microelectronic device applications such as high-K materials and gate dielectrics.[7] Results of these studies have shown Ta_2O_5 and TiO_2 thin films to possess, in addition to a high dielectric constants, low dielectric loss, leakage currents, and defect densities. However, few reports exist relative to the potential of using such buffer layers for tunable microwave applications.[4]

In this letter, we report the influence of ALD-grown Ta_2O_5 and TiO_2 buffer layers on the tunability and dielectric loss of BST thin films grown onto Si substrates. 50-nm-thick Ta_2O_5 and TiO_2 buffer layers were deposited onto Si substrates using penta-dimetylamino tantalum ($[Ta(NMe_2)_5]$; PDMAT) and water at 250 °C and titanium ethoxide $[Ti(OCH_2CH_3)_4]$ and water at 220 °C, respectively. (100) *n*-type Si substrates with resistivity of $\rho=10\ \Omega$ cm were etched in 10% HF solution for 1 min to remove the native oxide and treated by ozone to increase nucleation sites. PDMAT and titanium ethoxide were held at 85 and 90 °C, respectively, to achieve desired vapor pressures. The water was maintained at 20 °C. One cycle consists of injection of PDMAT or titanium ethoxide, purging with nitrogen, injection of water, and then purging with nitrogen. Each buffer layer was grown by repeating the above-mentioned cycles until the desired thickness was achieved. In order to improve the crystallinity and electrical properties of the TiO_2/Si and Ta_2O_5/Si structures, the buffer layers were annealed at 700 and 800 °C, respectively, in an oxygen atmosphere for 30 min. After annealing the buffer layer, $Ba_{0.6}Sr_{0.4}TiO_3$ thin films 500 nm thick were grown onto the Ta_2O_5(50 nm)/Si and TiO_2(50 nm)/Si substrates by pulsed laser deposition

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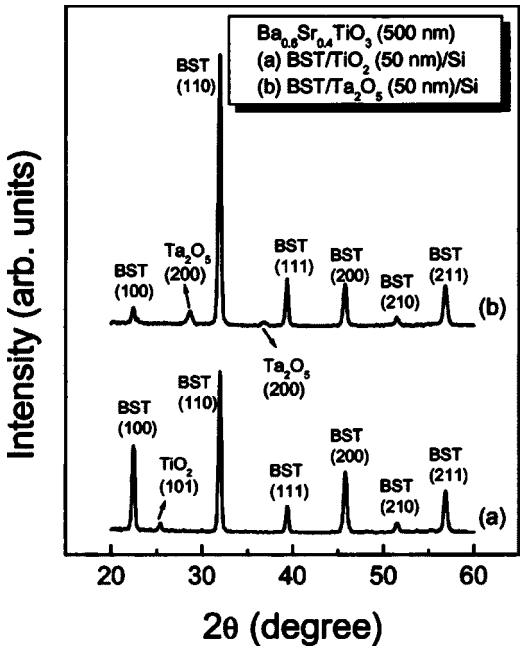

FIG. 1. X-ray diffraction patterns of BST films grown on (a) TiO_2/Si and (b) Ta_2O_5/Si substrates.

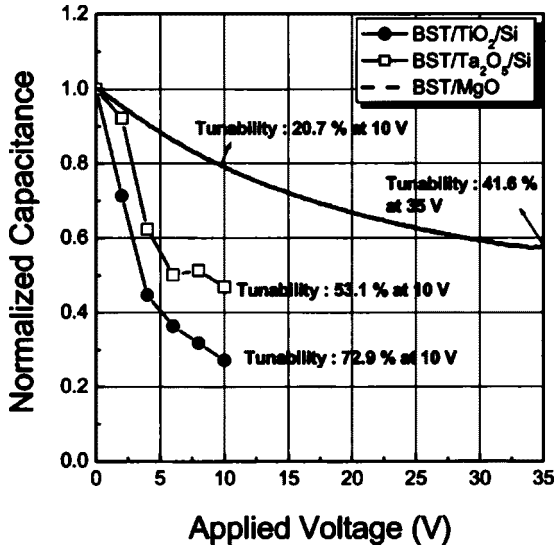

FIG. 2. Normalized capacitance of BST films grown on MgO, TiO_2/Si, and Ta_2O_5/Si substrates.

(PLD). The substrate temperature and oxygen ambient pressure during PLD were 750 °C and 50 mTorr, respectively. Laser ablation was carried out at a laser fluence of 1.5 J/cm^2 and a repetition rate of 5 Hz using a KrF excimer source ($\lambda = 248$ nm). A 200 nm Pt electrode was deposited onto the BST film to complete the circuit fabrication. To enhance the adhesion between the BST thin film and the platinum electrode, a thin Ti adhesion layer (25 nm) was deposited prior to Pt deposition. The IDC (interdigital capacitor) structure was designed to have 10 pairs of fingers 50 μm wide and 1000 μm long each spaced 50 μm apart. The crystallinity and the structure of the BST films were determined by x-ray diffractometry (XRD, Rigaku D/max-rc) excited with Cu $K\alpha$ radiation. The microstructure and roughness of the BST films was investigated by atomic force microscopy (AFM). The low-frequency tuning properties of BST films were measured with an HP 4194A impedance analyzer at a frequency of 100 kHz.

Figure 1 shows the XRD patterns of 500 nm BST films grown on TiO_2/Si and Ta_2O_5/Si substrates, respectively. The BST film on TiO_2/Si showed typical polycrystalline perovskite BST. In contrast to the film grown on TiO_2, the BST film deposited on Ta_2O_5/Si had highly (110) preferred orientation. X-ray diffraction also showed that the Ta_2O_5 and TiO_2 films became single phase crystalline following annealing (not shown).

The tuning properties of BST films at 100 kHz were investigated by examining interdigital capacitors with configurations Pt/Ti/BST/Ta_2O_5/Si and Pt/Ti/BST/TiO_2/Si. Figure 2 shows the normalized capacitance dependence of the BST thin films grown on Ta_2O_5/Si, TiO_2/Si, and MgO substrates as a function of bias voltage from 0 to 35 V. In general, tunability % is defined as $[(\epsilon_{max}-\epsilon_{min})/\epsilon_{max}]$, where ϵ_{max} and ϵ_{min} are the maximum and minimum permittivities within the voltage range examined. At an applied voltage of 10 V, the tunability values of BST films grown on Ta_2O_5/Si and TiO_2/Si were 53.1% and 72.9%, respectively. These values are much larger than that of BST films grown on a MgO single crystal substrate (20.7%, at 10 V). BST films grown on MgO single crystal substrates showed highly (100) preferred orientation and reached a tunability of only 41.6% with a much higher applied voltage of 35 V. The measured capacitance of BST grown on TiO_2/Si, Ta_2O_5/Si, and MgO substrates at zero bias voltage was 125.8, 30.8, and 9.95 pF, respectively. In comparison to parallel-plate capacitors, coplanar designs generally require higher control voltages and offer lower tunability, potential disadvantages of the IDC structure. The drive voltage needed to obtain appropriate tunability is very high in the BST/MgO structure given the low dielectric constant of the MgO single crystal substrate. Improved tunability and, thus, higher frequency tuning agility, has been shown to be possible in this study by incorporating TiO_2 or Ta_2O_5 buffer layers which increase the overall average dielectric constant and thereby minimize electric field attenuation in coplanar designs as found in the interdigital capacitor structures.[8] If we assume that we can ignore the formation of a SiO_2 layer between Si and the buffer layer during the annealing process in the case in which a high-K buffer layer is utilized, then the measured capacitance, $C_{measured}$ can be evaluated from the series connection of the bulk film capacitance, C_{bulk}, and buffer layer capacitance, C_{buffer}:

$$\frac{1}{C_{measured}} = \frac{1}{C_{bulk}} + \frac{1}{C_{buffer}}. \quad (1)$$

Thus, the average dielectric constant ($\epsilon_{average}$) can be expressed by

$$\frac{d_{total}}{\epsilon_{average}} = \frac{d_{bulk}}{\epsilon_{bulk}} + \frac{d_{buffer}}{\epsilon_{buffer}}, \quad (2)$$

where d_{total} d_{bulk} d_{buffer} are the total film thickness, bulk BST film thickness, and buffer layer thickness, respectively. The increased capacitance of BST films grown on TiO_2/Si and Ta_2O_5/Si compared with BST film grown on MgO substrate can be understood by examination of Eqs. (1) and (2).

In addition, high permittivity buffer layers with low loss tangents can minimize the power loss via the Si substrates.[4] The dielectric constant of Ta_2O_5 films is reported to be 25. In ALD grown TiO_2 layers, the dielectric constant was 100. The

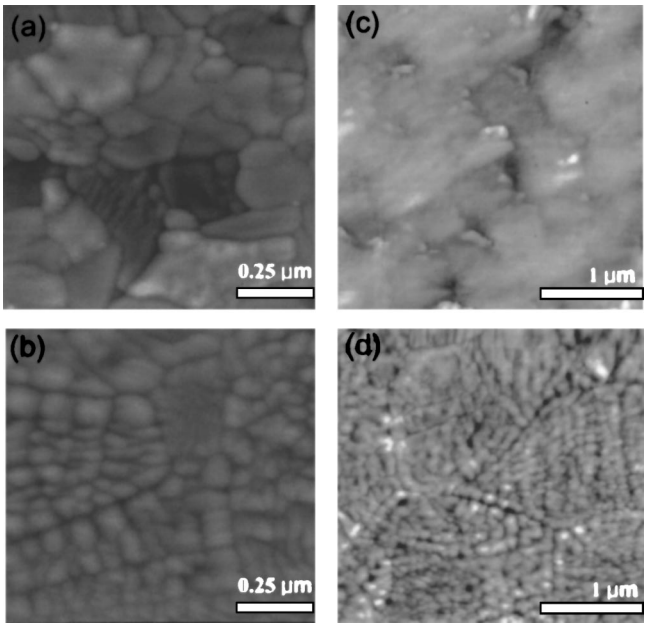

FIG. 3. AFM images of surface morphology for (a) 700 °C annealed TiO_2/Si, (b) 800 °C annealed Ta_2O_5/Si, (c) $BST/TiO_2/Si$, and (d) $BST/Ta_2O_5/Si$ structures.

advantages of using a TiO_2 layer are twofold; increased tunability of the BST film and minimized power loss via the Si substrate, consistent with Fig. 2. Figure 3 shows the surface morphologies of Ta_2O_5 and TiO_2 films on Si substrates. Ta_2O_5 on Si exhibited a roughness value of 3.57 nm rms and TiO_2 a value of 5.12 nm. As shown in Figs. 3(a) and 3(b), larger grain growth was observed in the TiO_2 as compared to the Ta_2O_5 film. The Ta_2O_5 buffer layer showed a uniform matrix of round and dense grains. The change in surface roughness and grain size distribution can affect the nucleation and subsequent grain size of BST thin films. Two-dimensional atomic force microscopy images of BST films prepared on Ta_2O_5/Si and TiO_2/Si substrates are shown in Figs. 3(c) and 3(d). Roughness values were 1.81 nm for $BST/Ta_2O_5/Si$ and 2.28 nm for $BST/TiO_2/Si$. The slightly higher BST film roughness on TiO_2/Si presumably originated from the greater roughness of the annealed TiO_2 layer as compared with that of the annealed Ta_2O_5 on Si. The lager grains in BST films grown on TiO_2/Si are likely the source of the increased tunability.

For microwave device applications, Si is normally not viewed as being compatible given its high dielectric losses at microwave frequencies. Figure 4 shows the loss tangent of BST films grown on MgO, TiO_2/Si, and Ta_2O_5/Si substrates, respectively. BST films grown on MgO showed, as expected, the lowest loss tangent. The loss tangent of BST grown on TiO_2/Si and Ta_2O_5/Si is high, presumably due to the lossy Si substrate. The figure of merit (FOM), ratio of tunability to dielectric loss, is very important for microwave

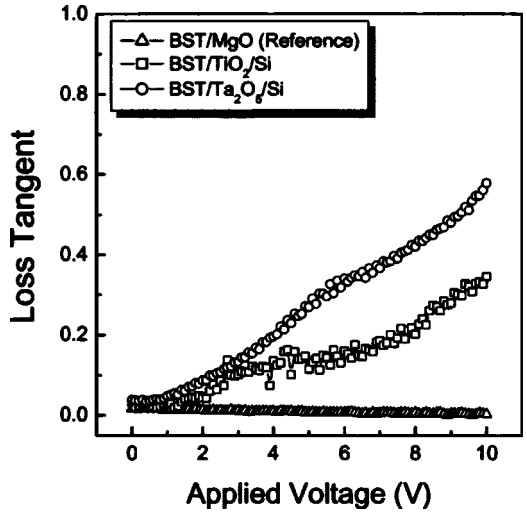

FIG. 4. Loss tangent of BST film grown on MgO, TiO_2/Si, and Ta_2O_5/Si substrates.

tunable device applications. At an applied voltage of 5 V, the FOM of BST/TiO_2 and BST/Ta_2O_5 were 5.22 and 1.57, respectively. The BST films grown on TiO_2 and Ta_2O_5 buffered Si substrates showed relatively lower FOM values as compared to the FOM (11.87) of BST/MgO due to the lossy Si substrate in the former case. To reduce the loss tangent, one can increase the buffer layer thickness or use a higher resistance substrate. Further studies are under way for the integration of BST microwave devices using GaAs, SiO_2/Si, and high resistivity Si substrates (more than 10 kΩ cm).[7] In summary, TiO_2 and Ta_2O_5 films, as buffer layers for the integration of BST films, were grown onto Si substrates by atomic layer deposition. BST films grown on TiO_2/Si and Ta_2O_5/Si by PLD showed remarkably high tunability at low applied voltage. This work demonstrates the potential feasibility of integrating BST films as microwave interdigital capacitors and/or coplanar waveguide tunable devices by use of thin film buffer layers of TiO_2 and Ta_2O_5.

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[1]B. Acikel, T. R. Taylor, P. J. Hansen, J. S. Speck, and R. A. York, IEEE Microw. Wirel. Compon. Lett. **12**, 237 (2002).
[2]H. S. Kim, M. H. Lim, H. G. Kim, and I. D. Kim, Electrochem. Solid-State Lett. **7**, J1 (2004).
[3]A. Vorobiev, P. Rundqvist, K. Khamchane, and S. Gevorgian, Appl. Phys. Lett. **83**, 3144 (2003).
[4]M. W. Cole, P. C. Joshi, M. Ervin, M. Wood, and R. L. Pfeffer, J. Appl. Phys. **92**, 3967 (2002).
[5]A. H. Meuller, N. A. Suvorova, A. Irene, O. Auciello, and J. A. Schultz, Appl. Phys. Lett. **80**, 3796 (2002).
[6]B. S. Lim, A. Rahtu, and R. G. Gordon, Nat. Mater. **2**, 749 (2003).
[7]X. H. Liu, Z. G. Liu, Y. P. Wang, T. Zhu, and J. M. Liu, Appl. Phys. A: Mater. Sci. Process. **76**, 197 (2003).
[8]H. T Lue, T. Y. Tseng, and G. W. Huang, J. Appl. Phys. **91**, 5275 (2002).