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Thickness effects on the electrical characteristics of $Ba_{0.7}Sr_{0.3}TiO_3$ capacitors with nano-Cr interlayer

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A multilayer $Ba_{0.7}Sr_{0.3}TiO_3/Cr/Ba_{0.7}Sr_{0.3}TiO_3$ (BST/Cr/BST) structure was sputtered sequentially onto $Pt/Ti/SiO_2/Si$ substrate. With the insertion of a 2 nm Cr interlayer, the temperature coefficient of capacitance of the BST/Cr/BST dielectric is about 69% lower than that of BST monolayer dielectric. The dielectric constant and dissipation factor as the function of Cr thickness are studied. X-ray diffraction patterns, the analysis results of energy dispersive spectroscopy, and the survey scan profiles of Auger electron spectroscopy reveal the formation of a TiO_2 secondary phase after the multilayer is annealed at 800 °C in O_2 atmosphere. The insertion of nano-Cr interlayer improves the electrical properties of BST capacitors. [DOI: 10.1063/1.2717553]

$Ba_xSr_{1-x}TiO_3$ (BST) films are extensively investigated for applications as integrated charge-storage dielectric and electric-field tunable elements for high frequency devices. BST thin films with considerably high dielectric constant can provide the sufficient storage charge. BST films also show the low leakage current, high breakdown field, high time-dependent dielectric breakdown, and low fatigue and aging effects.[1–3] However, the dielectric behaviors of BST films are very temperature sensitive, and this causes crucial concern in using BST capacitors for dynamic random access memory applications.[4,5]

It is well known that the grain size, dielectric constant, and leakage current of the BST thin films can be modified with an underlayer and/or with appropriate dopants.[6–9] This is ongoing research. Our previous work indicates that the insertion of a Cr interlayer lowers the leakage current and temperature dependence of capacitance of the BST capacitor.[4,5] However, the role that the nano-Cr interlayer plays on the dielectric properties of the BST films is unclear. In this study, the effects of thickness of Cr interlayer on the dielectric properties of the BST capacitors are investigated, and the root causes for the improvement of the dielectric behavior are explored.

Metal-insulator-metal (MIM) capacitors with $Pt/Ba_{0.7}Sr_{0.3}TiO_3/Cr/Ba_{0.7}Sr_{0.3}TiO_3/Pt$ structure were employed in this study. The starting *p*-type Si (100) wafers were cleaned by the standard RCA cleaning process. After the cleaning process, 100 nm SiO_2 films were grown on the Si substrate. 10 nm Ti films were sputtered onto the SiO_2 layer. The bottom electrodes, 100 nm Pt films, were dc sputtered at room temperature. The first $Ba_{0.7}Sr_{0.3}TiO_3$ (BST) films were then deposited using a rf magnetron sputtering at a substrate temperature of 350 °C. The sputtering chamber was evacuated to a base pressure of 1×10^{-5} torr initially. Then, BST films were deposited at a constant pressure of 5×10^{-3} torr which was maintained by a mixture of argon and oxygen at 9 and 3 SCCM (SCCM denotes cubic centimeter per minute at STP), respectively. The rf power for the deposition of both the first and second BST layers was 120 W (power density was 2.7 W/cm^2), and the total thickness of BST films was about 300 nm. Chromium films with various thicknesses were deposited with the same sputtering system without breaking the vacuum at the dc power of 100 W. The nominal Cr thicknesses were 2, 5, 10, and 15 nm and were monitored by the quartz crystal and the controller. The second BST films were then deposited. The BST/Cr/BST/Pt multilayer specimens were annealed at 800 °C in O_2 for 1 h and then were bombarded by O_2 plasma for 10 min before deposition of the top Pt electrode.

The phase of the films was characterized by an x-ray diffractometer (XRD) (RU-H3R, Rigaku, Japan). The high resolution transmission electron microscopy (TEM) (JEM-3000F, JEOL Ltd., Japan) was employed to observe the cross section of multilayer specimens and to measure the film thickness, and energy dispersive spectroscopy (EDS) was used to identify the elemental compositions of the specimens. The film compositions were also investigated by Auger electron spectroscopy (AES) (Microlab 350, Thermal VG Scientific Co., England). An *LCR* meter (HP-4285, Hewlett Packard Co., USA) was employed to measure the dielectric properties of the samples in the temperature range from 25 to 125 °C.

The x-ray diffraction patterns of the 800 °C annealed BST films with nano-Cr interlayer of various thicknesses are given in Fig. 1. All BST films show crystallized cubic phase. However, a diffraction peak appears at $2\theta=29.73°$, and this peak is identified as the (401) TiO_2 peak. The insertion of Cr layer affects the texture of the BST films. As indicated in the inset of Fig. 1, the peak ratio $I(100)/I(110)$ of BST films increases from 8.5% of the mono-BST layer to 21.3% for BST with a 2 nm Cr interlayer and then decreases when the Cr thickness is larger than 2 nm. The 2 nm nominal film is discontinuous,[5] while the 15 nm nominal Cr film shown in Fig. 2(a) is continuous, and the measured thickness is around

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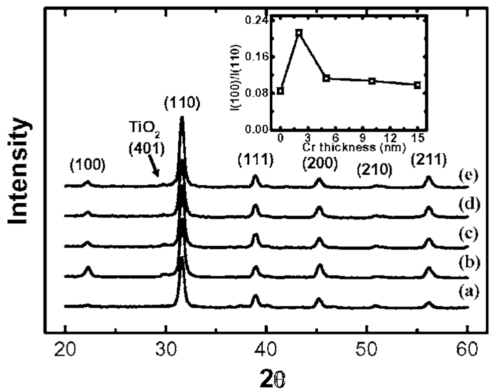

FIG. 1. X-ray diffraction patterns of BST annealed at 800 °C in O_2 with and without the insertion of nano-Cr interlayer: (a) mono-BST layer, (b) BST/Cr(2 nm)/BST, (c) BST/Cr(5 nm)/BST, (d) BST/Cr(10 nm)/BST, and (e) BST/Cr(15 nm)/BST. Inset is the ratio of $I(100)/I(110)$ as a function of Cr thickness.

18 nm. That the continuity or discontinuity of Cr film affects the stress in the films may influence the texture of the BST films. The preferred (100) orientation enhances both the dielectric constant and the tunability of the BST because the Ti ion preferentially displaces along the (100) direction towards the oxygen ions.[10]

Figure 2 shows the TEM cross-section view and EDS analysis results of the BST/Cr(15 nm)/BST/Pt structure. The inset in Fig. 2(e) shows AES survey scan profiles for the surface of the specimen. Formation of a thin TiO_2 layer for BST/Cr/BST/Pt is observed, as indicated in Fig. 2(e), and confirmed with the XRD results shown in Figs. 1(b)–1(e).

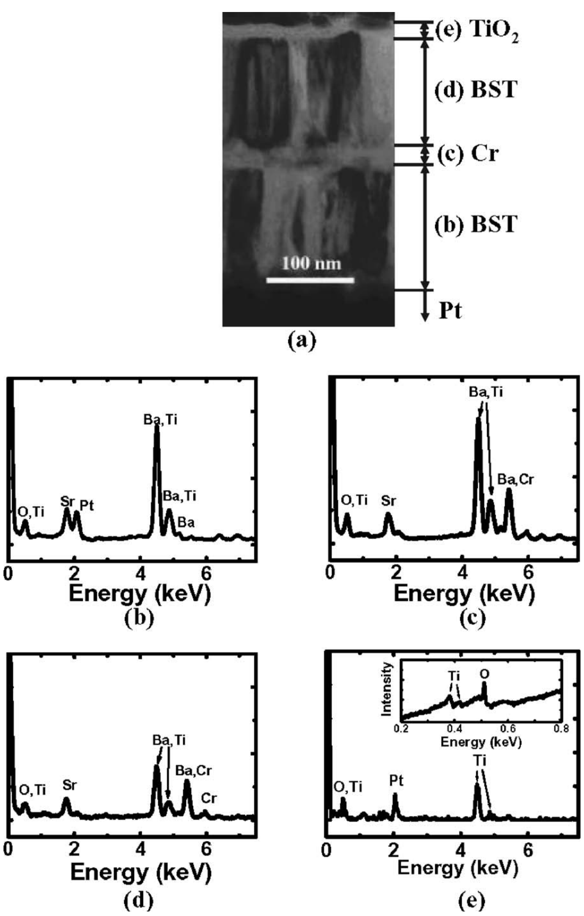

FIG. 2. (a) TEM cross-section view the BST/Cr(15 nm)/BST MIM capacitor. EDS spectra of (b) BST bottom, (c) Cr interlayer, (d) BST upper, and (e) TiO_2 phase. The inset of (e) shows AES survey scan profile for the surface of BST/Cr/BST.

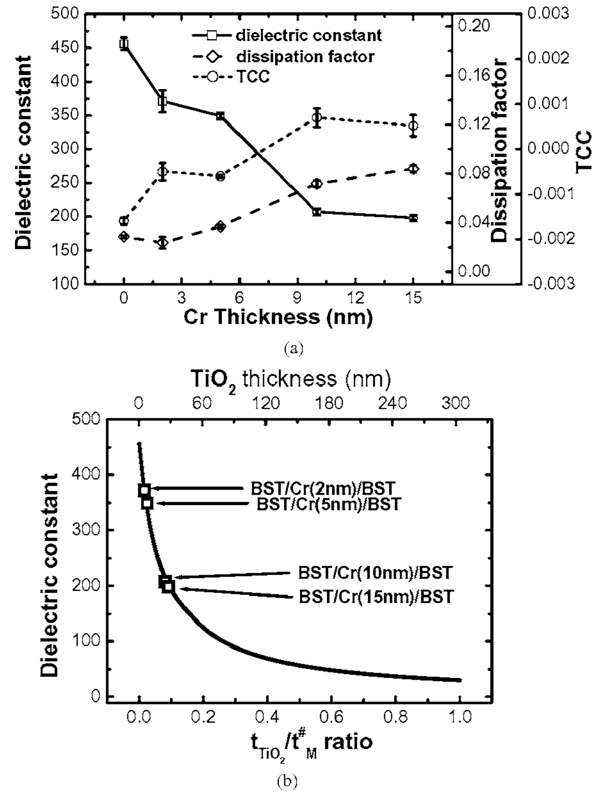

FIG. 3. (a) Dielectric constant, dissipation factor, and temperature coefficient of capacitance with nano-Cr interlayer of various thicknesses and mono-BST layer. (b) Calculated dielectric constants vs t_{TiO_2}/t_M ratio and TiO_2 thickness are calculated based on the serial model (Ref. 11). The measured dielectric constants of the BST/Cr/BST capacitors in this work are also shown. t_M is the thickness of the BST/Cr/BST sample.

The 100 kHz dielectric constant (k) and dissipation factor of specimens with Cr films of various thicknesses are presented in Fig. 3(a). The dielectric constant decreases with the increase of the Cr interlayer thickness. The dissipation factor decreases initially and then increases as the thickness of Cr increases. A minimum dissipation factor of ~0.023 is obtained for specimens with 2 nm Cr. As stated previously, a preferred (100) orientation enhanced the dielectric constant of the BST films, and specimen with 2 nm Cr has enhanced (100) orientation as compared to those without Cr. However, the dielectric constant of specimen with 2 nm Cr (i.e., 371) is smaller than that of the specimen without Cr (i.e., 456). It is argued that the decrease of the dielectric constant for Cr-containing specimen is attributed to the formation of the TiO_2 layer. The dielectric constants of mono-TiO_2 and mono-BST are 20 and 456, respectively. The curve in Fig. 3(b) is the calculated dielectric constants of BST/Cr/BST in series with TiO_2 layers of various thicknesses.[11] Also shown in Fig. 3(b) is the measured dielectric constant. On the basis of the calculated dielectric constant curve, the thickness of TiO_2 films ranges from 4.8 to 23.4 nm. The temperature coefficient of capacitance (TCC) is defined as

$$\mathrm{TCC} = \frac{C_T - C_{T_r}}{(T - T_r)C_{T_r}},$$

where T is the temperature of interest (125 °C in this study), T_r is the temperature of reference (25 °C in this study), and

C_T and C_{T_r} are the capacitances measured at T and T_r, respectively. A TCC of $-5.0\times10^{-4}/\,^\circ\mathrm{C}$ is obtained for capacitors with 2 nm Cr as compared to that of $-1.60\times10^{-3}/\,^\circ\mathrm{C}$ for capacitors with BST monolayer, as indicated in Fig. 3(a). Insertion of nano-Cr interlayer improves the temperature stability of the BST dielectric, and a positive TCC is observed for specimens with thicker than 10 nm Cr. The negative TCC of BST is compensated by the positive TCC of the TiO_2.[12] It is believed that the formation of the TiO_2 films affects the dielectric constant, dissipation factor, and TCC of the specimens. The thermal stability of the dielectric is enhanced with the implementation of the nano-Cr interlayer. However, the mechanism for the formation of TiO_2 in the presence of nano-Cr interlayer is subjected to further study.

In summary, the MIM capacitors with BST/Cr/BST multilayer dielectric are investigated. The insertion of the 2 nm Cr improves both the dissipation factor and TCC of the capacitors. A TCC of $-5.0\times10^{-4}/\,^\circ\mathrm{C}$ from 25 to 125 °C is obtained for BST/Cr/BST as compared to that of $-1.60\times10^{-3}/\,^\circ\mathrm{C}$ for mono-BST films. Besides, a dissipation factor of 0.023 at 100 kHz is obtained for BST/Cr/BST capacitors as compared to that of 0.028 for mono-BST capacitor. Although the dielectric constant decreases from 456 to 371 with the implementation of the 2 nm Cr layer, the temperature stability of the capacitor is improved. Formation of a TiO_2 layer in series with the BST/Cr/BST structure is argued to be one of the reasons for the change in the electrical characteristics of the capacitors.

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