Influence of Ba/Sr ratio in compressively-strained (Ba,Sr)TiO3(001) films on the ferroelectric phase transition

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In this paper, we investigated the Ba/Sr ratio dependence of the ferroelectric phase transition temperature of BST (Ba,Sr)TiO3 films with different Ba/Sr ratio on SrTiO3 substrates. The in-plane compressive strain shifts the ferroelectric phase transition to higher temperatures; however, the magnitude of its impact varies by the Ba/Sr ratio. With increasing the Ba/Sr ratio, the sensitivity to the strain becomes larger, which can be associated with the compositional dependence of the Weiss constant, electrostrictive constant and elastic constant of BST.

Key-words : Barium strontium titanate, Strain, Ferroelectric phase transition

1. Introduction

(Ba,Sr)TiO3 [BST] is known for the large dielectric constant, relatively low dielectric loss and large dielectric tunability by applying an electric field. It is also well known that the ferroelectric phase transition temperature, where the dielectric constant is peaking in its temperature dependence, can be widely modified by changing the Ba/Sr ratio. Therefore, BST has been considered as a potential thin film material used in small dielectric devices such as dynamic random access memories and RF-tunable thin film capacitors. However, it has been theoretically and experimentally shown that the strain in BST films varies the ferroelectric phase transition temperature too; thus, one has to control both the Ba/Sr ratio and the strain in order to achieve the desired dielectric property of BST films.

In this paper, we investigated the Ba/Sr ratio dependence of such a strain effect by comparing the ferroelectric phase transition temperature of the (001)-epitaxial BST films with different Ba/Sr ratio and strain. We show that there is an appreciable difference in the sensitivity to the strain for different Ba/Sr ratio.

2. Experimental

BST (x = 0.3, 0.5 and 0.7) films were deposited on (001) SrTiO3 and (001) SrRuO3(/001) (La,Sr)(Al,Ta)O3 by RF magnetron sputtering. Regardless of the Ba/Sr ratio, the in-plane compressive strain shifts the ferroelectric phase transition to higher temperatures; however, the magnitude of its impact varies by the Ba/Sr ratio. With increasing the Ba/Sr ratio, the sensitivity to the strain becomes larger, which can be associated with the compositional dependence of the Curie-Weiss constant, electrostrictive constant and elastic constant of BST.

The in-plane compressive strain was controlled by the difference in the lattice constant of different substrates. In this study, BST films were deposited on (001) SrTiO3 and (001) SrRuO3(/001) (La,Sr)(Al,Ta)O3 by RF magnetron sputtering. Regardless of the Ba/Sr ratio, the in-plane compressive strain shifts the ferroelectric phase transition to higher temperatures; however, the magnitude of its impact varies by the Ba/Sr ratio. With increasing the Ba/Sr ratio, the sensitivity to the strain becomes larger, which can be associated with the compositional dependence of the Curie-Weiss constant, electrostrictive constant and elastic constant of BST.

The structural properties of the films were characterized by X-ray diffraction (XRD) using four-axis diffractometers (Philips X’Pert MRD and Bruker D8 DISCOVER) with Cu Kα1 radiation. For dielectric measurements, 15 μm square Pt top electrodes were fabricated by RF magnetron sputtering and following lift-off process. A precision LCR meter (HP 4194A) with an oscillation level of 20 mV was employed for the measurements of the dielectric constant at 10 kHz-1 MHz. In this study, no significant frequency dispersion of the dielectric constant was observed in the examined frequency range.
films with $x = 0.3$, 0.5 and 0.7 deposited on SrRuO$_3$/SrTiO$_3$ substrates at the growth rate of 29, 31 and 16 nm/h, respectively. As can be seen, the in-plane lattice spacing of the BST films is close to that of SrTiO$_3$; namely, these films are strongly constrained with large in-plane compressive strain of $\theta_0$ = 0.006, 0.009 and 0.012 for $x$ = 0.3, 0.5 and 0.7, respectively.12)

Figure 2 plots the temperature dependence of the out-of-plane dielectric constant measured at 100 kHz for the strongly in-plane compressed films on SrRuO$_3$/SrTiO$_3$ shown in Fig. 1. As can be seen in the figure, the temperatures for the maximum dielectric constant of BST films is close to that of SrTiO$_3$; namely, these films are strongly constrained with large in-plane compressive strain of $\theta_0$ = 0.006, 0.009 and 0.012 for $x$ = 0.3, 0.5 and 0.7, respectively.12)

The comprehensive comparison of $\Delta T_0$ for various films having different Ba/Sr ratio and strain is needed to clarify the Ba/Sr ratio dependence of the strain effect.

In order to fabricate the films with various strains, we utilized the difference in the lattice mismatch and the degree in the relaxation from the mismatch. The former is to deposit the films on different substrates, namely, SrRuO$_3$/SrTiO$_3$ and SrRuO$_3$/LSAT in this study. As described above, the lattice mismatch between BST and SrRuO$_3$/LSAT is smaller than that between BST and SrRuO$_3$/SrTiO$_3$. Therefore, the BST films deposited on SrRuO$_3$/LSAT are less strained. The latter is to deposit the films with different thickness or at different growth rate. Especially, the slower growth rate effectively relaxes the strain of the epitaxial films. Indeed, the BST films with $x = 0.7$ deposited on SrRuO$_3$/SrTiO$_3$ at the growth rate of 3 and 5 nm/h were greatly relaxed.10)

Figure 3 shows the XRD $\theta$–$2\theta$ scans around 200 peaks of (Ba$_{x}$Sr$_{1-x}$)$_2$TiO$_5$ [BST] films ($x$ = 0.3, 0.5 and 0.7) with various strains. Solid thin lines show the $2\theta$ angle of unstrained bulk BSTs for $x$ = 0.3, 0.5 and 0.7.

The Ba/Sr ratio has a larger lattice constant, namely, a larger lattice mismatch between BST and SrRuO$_3$/SrTiO$_3$ substrate. Therefore, the comprehensive comparison of $\Delta T_0$ for various films having different Ba/Sr ratio and strain is needed to clarify the Ba/Sr ratio dependence of the strain effect.
Figure 4 shows the shift of the ferroelectric phase transition temperature divided by the absolute value of the in-plane strain, $\Delta T_0/|u_i|$, for compressively-strained (Ba,Sr)TiO$_3$ [BST] films with x = 0.3, 0.5 and 0.7 (circle). The results give us an additional guide for controlling the dielectric properties of the BST(001) films.

4. Conclusions

By growing the epitaxial BST films on (001),SrRuO$_3$/ (001)SrTiO$_3$ and (001),SrRuO$_3$/ (001)LSAT by RF magnetron sputtering, the BST(001) films having different in-plane compressive strains were fabricated. The in-plane compressive strain shifts the ferroelectric phase transition temperature $T_0$ higher than that of unstrained bulk BSTs as can be theoretically expected. In addition, it was found that the shift of $T_0$ is larger for the films with larger Ba content. The large sensitivity to the strain of BST films with Ba rich composition can be associated with the compositional dependence of $|C_1|$, $|Q_{12}|$ and $|S_{11}| + |S_{12}|$. The obtained results give us an additional guide for controlling the dielectric properties of the BST(001) films.

Acknowledgements This work was partially supported by Grants-in-Aid for Scientific Research (20800306, 22760510), Japan.

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