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Effects of deposition temperature on the crystallinity of $Ba_{0.5}Sr_{0.5}TiO_3$ epitaxial thin films integrated on Si substrates by pulsed laser deposition method

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Abstract

Epitaxial $Ba_{0.5}Sr_{0.5}TiO_3$ (BSTO) thin films were grown on TiN buffered Si (0 0 1) substrates by PLD method and the effects of deposition temperature on their crystallinity and microstructure were studied. BSTO thin films were prepared with substrate temperature ranging from 350 to 650 °C. The BSTO films grown at below 400 °C showed amorphous phase and the film grown at 450 °C showed mixed phase of crystalline and amorphous, where crystalline phase was observed only at the top surface portion of the film. The BSTO films with fully crystalline phase were obtained in the samples deposited at above 500 °C. The (0 0 *l*) preferred orientation and the crystallinity of the BSTO films were improved with increasing the temperature. The dielectric constant, measured at 100 kHz and at room temperature, of the BSTO film grown at 650 °C was measured to be as high as 1129.

Keywords: A. Films; C. Dielectric properties; D. $BaTiO_3$ and titanates; E. Functional applications

1. Introduction

$Ba_xSr_{1-x}TiO_3$ (BSTO) thin films are very promising material for practical applications, such as phase shifters, delay lines, tunable filters, etc. [1,2] because they have high electric-field tunability and low dielectric loss. Therefore, a wide variety of deposition methods, such as pulsed laser deposition (PLD), RF-magnetron sputtering, metalorganic chemical vapor deposition (MOCVD), and chemical solution deposition (CSD) have been used for the preparation of BSTO thin films. Among them, PLD technique has been regarded as one of the most promising methods because of numerous advantages, including precise control of film stoichiometry close to the target, reproducibility, uniformity, and simplicity, so it has been widely used in preparing ferroelectric thin films.

For the growth of high quality epitaxial oxide thin films, oxide single-crystal substrates, such as $SrTiO_3$ [3], $LaAlO_3$ [4] and MgO [5], have been widely used because they have low lattice mismatch and similar crystal structure with film materials, which gives easy of fabrication. However, oxide substrates are expensive and incompatible with existing mature Si technology. Therefore, in practical viewpoint, it is more desirable to fabricate highly oriented or epitaxial oxide thin films on Si substrates to open the door to fabricate Si-based novel devices with enhanced functionality and flexibility. There have been many previous studies on oxide epitaxy on Si substrates. Various kinds of material systems, such as BTO [6], STO [7], CeO_2 [8], ZnO [9,10], and BTO/STO superlattices [11] have been prepared on Si substrates by various processing methods of MOCVD, PLD, and MBE technique.

In preparing oxide epitaxial thin films on Si substrates, various kinds of buffer layers, such as, SiC [9], AlN [10], CaF_2 [12] and TiN [7] have been used to avoid several major problems of possible oxidation of Si surface, interdiffusion at

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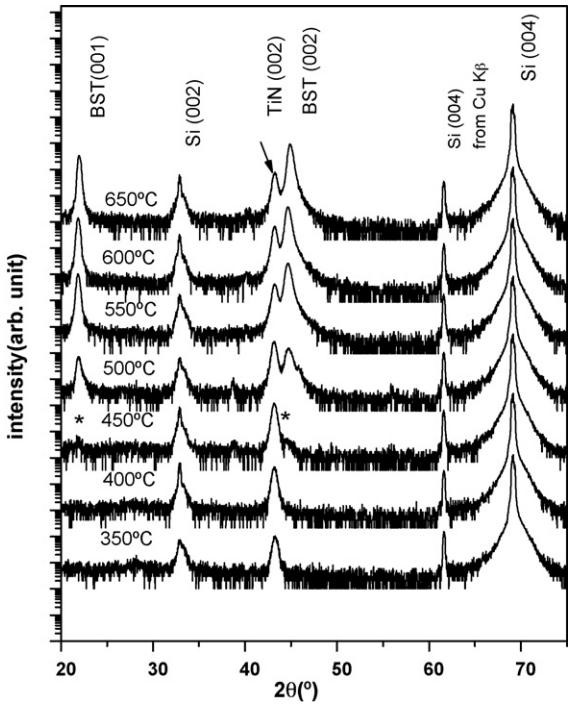

Fig. 1. XRD θ–2θ scans of BSTO thin films grown on TiN buffered Si substrates at various substrate temperatures ranging from 350 to 650 °C.

the interface, and large lattice mismatches between oxide films and Si substrates. Among them, TiN is the most promising candidate because it has very strong corrosion and erosion resistance, good diffusion resistance, low resistivity, and good adhesion property to most oxide materials [13]. In addition, the epitaxy nature of the TiN thin film on a Si substrate has been well known by domain matching epitaxy theorem even though they have very large lattice mismatch of 25% [13].

Therefore, the purpose of this study is to integrate epitaxial BSTO thin films on Si substrates using TiN buffer layer. $Ba_{0.5}Sr_{0.5}TiO_3$ thin films were prepared by PLD method at various substrate temperatures and the effects of growth temperature on the microstructure and crystallinity of PLD derived BSTO thin films are presented.

2. Experimental procedure

Epitaxial TiN and oxide thin films were fabricated on Si (0 0 1) substrates using a multitarget PLD system equipped with a high-vacuum chamber up to 7×10^{-6} Torr and a KrF excimer laser (λ = 248 nm). The stoichiometric polycrystalline TiN target (99.5%, CERAC, USA) and oxide target (BSTO), prepared by solid-state reaction of high-purity $SrCO_3$, $BaCO_3$, and TiO_2 powders (Sigma–Aldrich, USA), were ablated by KrF excimer laser. Si (0 0 1) substrates were ultrasonically cleaned in acetone, methanol, isopropyl alcohol, and deionized water

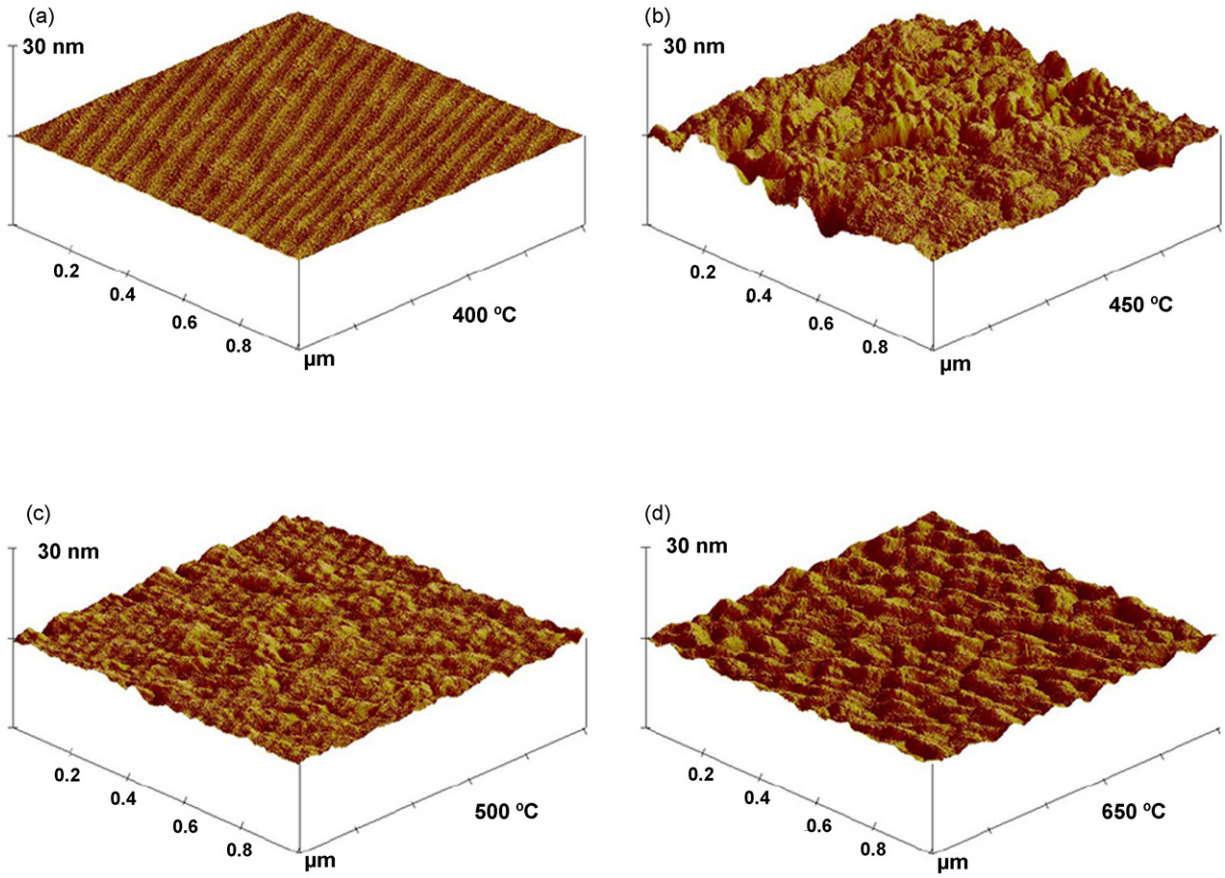

Fig. 2. Atomic force microscopy images of the BSTO thin films prepared at 400 °C (a), 450 °C (b), 500 °C (c), and 650 °C (d).

sequentially followed by dipping into 10 wt% HF solution for 1 min to remove the surface oxide layer. The cleaned substrate was loaded into the processing chamber immediately to minimize possible formation of native oxide. After loading the substrate into the chamber, the substrate was heated at a desired temperature at a base vacuum pressure 9×10^{-6} Torr. The target–substrate distance was kept at 40 mm. The laser repetition rate was 8 Hz for the TiN film and 10 Hz for BSTO films. Laser energy densities irradiated on the TiN and BSTO targets were 4.2 and 3 J/cm^2, respectively. The deposition temperature for the TiN buffer layer was 700 °C and for the BSTO thin films was ranging from 350 to 650 °C. The phase of the film was characterized using X-ray diffraction (XRD) (X'pert PRO, Philips, Eindhoven) operated at 40 kV and 30 mA. Microstructure, crystallographic orientation, epitaxy and roughness of the films were analyzed using conventional transmission electron microscopy (TEM) (JEM 2000EX, JEOL, Tokyo, Japan), high-resolution TEM (HRTEM) (Tecnai, FEI, Eindhoven, Netherland) and atomic force microscopy (AFM) (Nanoscope III, DI, Santa Barbara, USA). The relative dielectric constant of the $Ba_{0.5}Sr_{0.5}TiO_3$ thin films was measured using an impedance analyzer (HP4192A, HP, USA) at 100 kHz and at room temperature.

3. Results and discussion

Fig. 1 shows XRD θ–2θ scans of BSTO thin films grown on TiN buffered Si substrates at various substrate temperatures ranging from 350 to 650 °C using the PLD system. X-ray diffraction peaks from BSTO are not observed in the films prepared at below 400 °C, indicating that the films are amorphous. Very weak (0 0 l) peaks, indicated by "*", of the BSTO phase begin to appear in the diffraction spectrum of the BSTO thin film grown at 450 °C, which indicates that phase transformation has occurred in the BSTO film as the deposition temperature increases. It is clearly shown in Fig. 1a that the intensity of the (0 0 l) peaks for BSTO films increases and the full-width at half-maximum of (0 0 2) peaks decreases from 3.54 at 500 °C to 1.68 at 650 °C with increasing deposition temperature. This result indicates that the crystallinity and the (0 0 l) preferred out-of-plane orientation of BSTO films are improved with increasing the deposition temperature. The diffraction patterns show only {0 0 l} family of planes of BSTO indicating that the films are highly textured along the film normal. Off-axis XRD ϕ-scans of the BSTO {1 0 1} planes, TiN {1 0 1} planes, and Si {2 0 2} planes from the sample grown at 650 °C, not shown here, show in-plane orientation relationship of $[1\,0\,0]_{BSTO}||[1\,0\,0]_{TiN}||[1\,0\,0]_{Si}$ and $[0\,1\,0]_{BSTO}||[0\,1\,0]_{TiN}||[0\,1\,0]_{Si}$. XRD results of θ–2θ scans and off-axis ϕ-scans show the epitaxial orientation relationship of $[1\,1\,0](0\,0\,1)_{BSTO}||[1\,1\,0](0\,01\,)_{TiN}||[1\,1\,0](0\,0\,1)_{Si}$.

Fig. 2a–d are AFM images of the BSTO films prepared at 400, 450, 500 and 650 °C, respectively, which show the surface morphology of the BSTO films. The BSTO films prepared at 400 and 450 °C show very smooth surface (rms = 0.184 nm) and very rough surface (rms = 1.735 nm), respectively and the BSTO films prepared at above 450 °C shows the similar surface

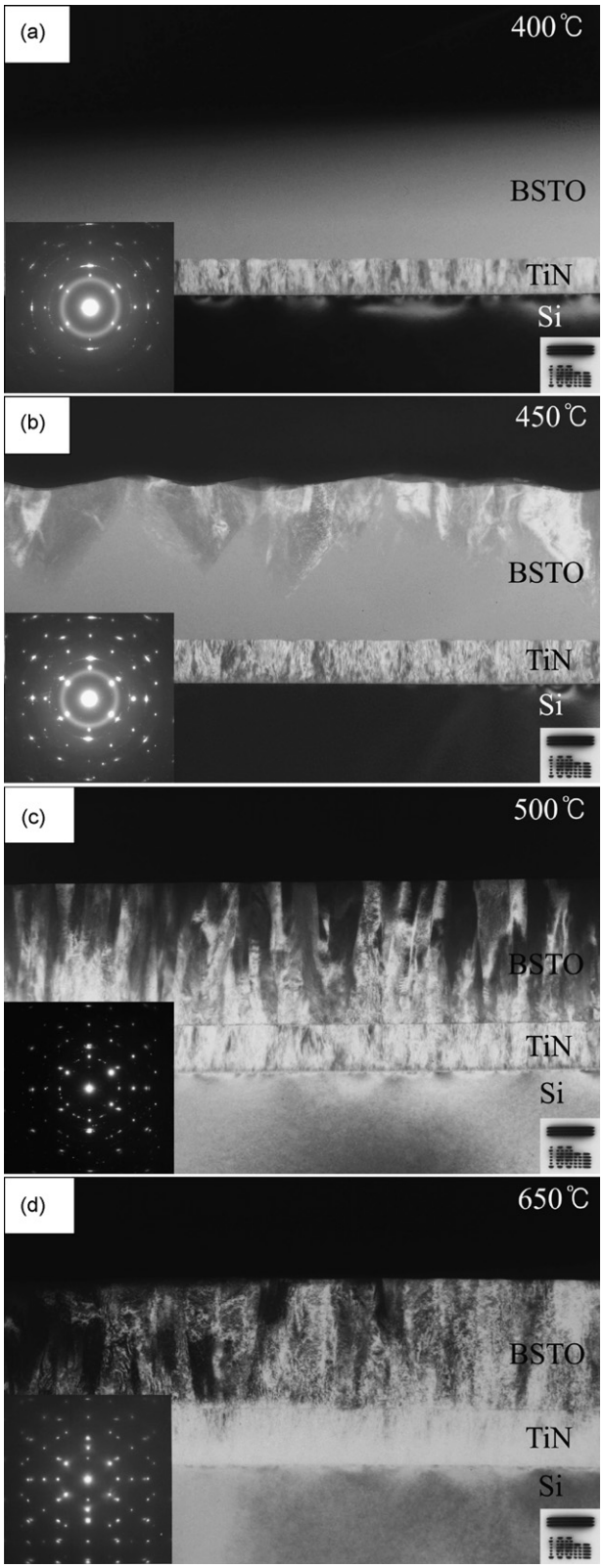

Fig. 3. Transmission electron microcopy bright-field images that show cross-sectional microstructure of BSTO/TiN/Si samples, where BSTO thin films were prepared at 400 °C (a), 450 °C (b), 500 °C (c), and 650 °C (d). Insets are corresponding selected area electron diffraction patterns obtained at film/substrate interfaces.

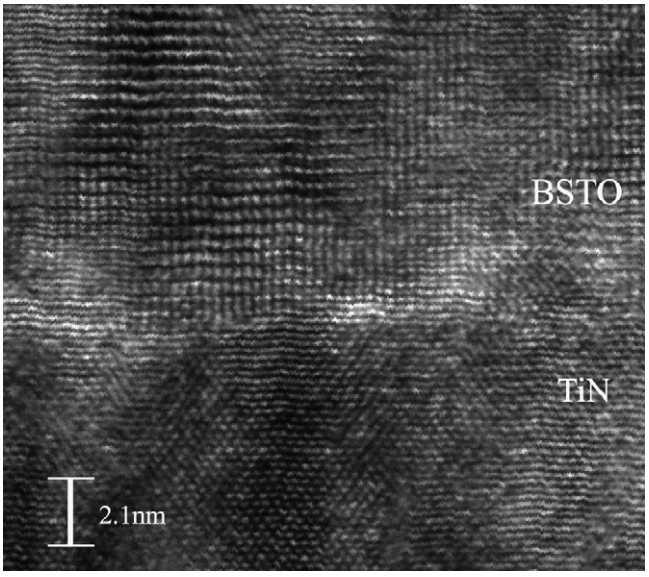

Fig. 4. High-resolution TEM micrograph showing the BSTO/TiN interface on an atomic level. The BSTO thin film was grown at 650 °C and at oxygen partial pressure of 1×10^{-4}.

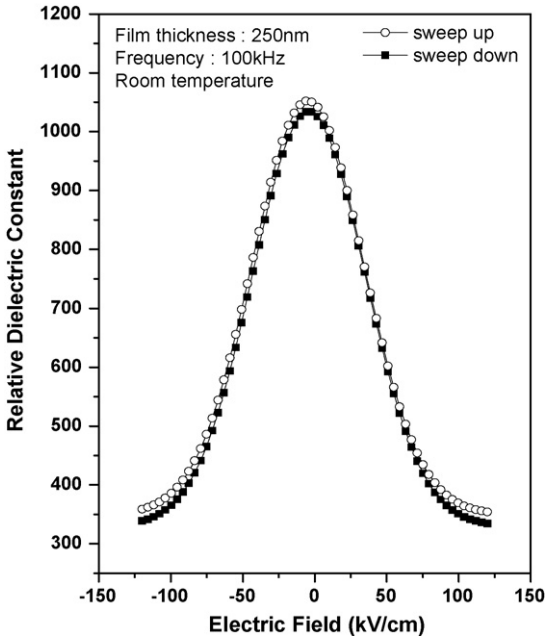

Fig. 5. DC electric field dependence of the dielectric constant for the BSTO thin film grown at oxygen partial pressure of 1×10^{-4} and substrate temperature of 650 °C.

roughness about ~0.789 nm. No remarkable changes in the surface roughness of the BSTO films prepared at above 500 °C were observed in this experiment.

Fig. 3a–d are TEM bright field images that show cross-sectional microstructures of BSTO/TiN/Si samples, where BSTO thin films were prepared at 400, 450, 500 and 650 °C, respectively. Insets are corresponding selected area electron diffraction patterns (SADPs) obtained at film/substrate interfaces. No contrast difference is observed in the BSTO film prepared at 400 °C (Fig. 3a) and the corresponding SADP shows a diffuse halo ring pattern, which indicates that the BSTO film prepared at 400 °C is amorphous phase. The diffraction spots in the SADP in Fig. 1a come from the TiN/Si substrates. This result is very well consistent with the XRD diffraction result in Fig. 1a where no diffraction peaks are observed in the BSTO thin film prepared at 400 °C. It is clearly observed in Fig. 3d that there are two distinct layers. Bright and dark contrast with very rough surface is observed in the top layer and no contrast change is observed in the bottom layer, which indicates that crystalline phase is formed at the top surface region and amorphous phase remains at the lower region of the BSTO film. Corresponding SADP shows mixture of spots and diffuse halo rings of BSTO phase. Fully crystallized BSTO films without any amorphous phase are observed in the BSTO samples prepared at above 500 °C (Fig. 3c and d). Corresponding SADPs also show no diffuse halo rings, indicating fully crystallized films. However, there is a difference in the microstructures and SADPs between the BSTO thin film grown at 500 °C and the BSTO thin film grown at 650 °C. Not only the microstructural images but also the diffraction patterns in Fig. 3c and d indicate that the BSTO thin film grown at 650 °C shows better crystallinity and epitaxy nature compared to the BSTO thin film grown at 500 °C. These results show that the crystallinity and epitaxy nature of the BSTO films improve with increasing the deposition temperature. It has been also observed by Chiu et al. [14] and Zhu et al. [15] that the preferred orientation and crystal quality of BSTO thin films improve with increasing the deposition temperature. Indexing of the SADP in Fig. 3d shows an epitaxial orientation relationship of $[1\ 1\ 0](0\ 0\ 1)_{BSTO}||[1\ 1\ 0](0\ 0\ 1)_{TiN}||[1\ 1\ 0](0\ 0\ 1)_{Si}$. This result is well consistent with the XRD results in Figs. 1. Fig. 4 is a high-resolution TEM micrograph showing the BSTO/TiN interface on an atomic level, where the BSTO thin film was grown at 650 °C. It is clearly shown that BSTO and TiN forms a quite sharp interface on an atomic level without any indication of interfacial reaction. This HRTEM image also shows that the BSTO was grown epitaxially from the BSTO/TiN interface at high temperature process.

Fig. 5 shows the electric field dependence of the dielectric constant for the BSTO film grown at oxygen partial pressure of 1×10^{-4} and substrate temperature of 650 °C, where the capacitance–voltage characteristics were measured at the frequency of 100 kHz and room temperature, while the electric field was swept from negative value (−125 kV/cm) to positive value (+125 kV/cm) and vice versa. The epitaxial BSTO thin film (~250 nm in thickness) shows a maximum dielectric constant of 1129 with no bias.

4. Conclusions

Epitaxial $Ba_{0.5}Sr_{0.5}TiO_3$ thin films were successfully prepared on Si substrates using a TiN buffer layer by the PLD method. BSTO thin films were grown with a cube-on-cube epitaxy nature which has an epitaxial orientation relationship of $[1\ 1\ 0](0\ 0\ 1)_{BSTO}||[1\ 1\ 0](0\ 0\ 1)_{TiN}||[1\ 1\ 0](0\ 0\ 1)_{Si}$. The BSTO thin films grown at below 400 °C showed amorphous phase and the BSTO thin film grown at 450 °C

showed mixed phase of crystalline and amorphous, and the BSTO thin films grown at above 500 °C showed fully crystalline phase. It was also found that the preferred orientation and the crystallinity of the BSTO thin films improved with increasing the growth temperature. The dielectric constant of the BSTO film grown at oxygen partial pressure of 1×10^{-4} Torr and at 650 °C was measured to be as high as 1129.

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