High tunability $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ thin films fabricated on Pt–Si substrates with $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ buffer layer

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Received: 7 April 2007 / Accepted: 19 June 2007 / Published online: 18 July 2007
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Abstract $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ (BST) thin films for the tunable microwave devices were grown using pulsed laser deposition (PLD) on Pt/Ti/SiO₂/Si (Pt–Si) substrates with $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (LSCO) buffer layers. For comparison, the films were also grown on Pt–Si substrates. X-ray diffraction results showed that the BST films on Pt–Si displayed a highly (110) preferred orientation, while the films with the LSCO buffer layers were (100)-oriented. Atomic force microscope (AFM) revealed that BST films with LSCO buffer layers had smoother surface and smaller grain size. Compared with (110) BST films, the (100) BST thin films had the higher tunability and the better figure of merit (FOM). The dielectric constant, the dielectric loss and the tunability of the BST thin films on LSCO/Pt–Si substrates measured at 10 kHz were 1010, 0.031 and 82.4%, respectively. Additionally, the current–voltage (I – V) measurement indicated that the leakage current density of (100) BST thin films on LSCO/Pt–Si substrates was reduced compared with that of (110) BST thin films directly on Pt electrodes, due to the possible reduction of interface oxygen vacancies at BST/LSCO interface and smaller grain size of the films. The enhancement in dielectric properties may be attributed to (100) preferred orientation in the films.

1 Introduction

Recently, ferroelectric thin films have been widely used in the tunable microwave devices, such as electrically tunable mixers, delay lines, filters, capacitors, oscillators, resonators and phase shifters [1–3]. BST thin films are regarded as a promising material for the replacement of traditional ferrite and semiconductor device, due to their unique physical characteristics of high dielectric constant, low dielectric loss, and tunable dielectric constant [4]. It is well known that the dielectric properties of BST thin films are influenced by many factors, such as the deposition method, composition, dopant, microstructure, interfacial quality, bottom electrodes, and thickness of the films [5–7]. Usually, some metals like platinum (Pt) with a high work function are employed as an electrode for the BST thin films because they can lead to a low leakage current density by building up a high Schottky barrier at BST/metal interfaces. However, some problems still existed, such as the formation of hillocks at high temperature [8] and amiability in oxygen diffusion, which greatly undermine the dielectric properties and hinder practical applications of BST thin films [9]. In addition, BST thin films directly deposited on Pt electrode are usually polycrystalline, which exhibit bad properties compared with preferred orientated films [10].

LSCO, which has a pseudocubic perovskite structure with a lattice constant of 3.835 Å, has been used as an oxide electrode [11]. There are low lattice mismatch and structural compatibility for the BST/LSCO structures, which are potential to improve dielectric properties of the films. Several research groups have reported that the properties of ferroelectric films could be improved by preferentially controlled orientation and stress state [12–14]. With LSCO films as buffer layer, the PMN–PT films

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with a dielectric constant of 3800 have been deposited on bare Pt/Ti/SiO₂/Si substrates [11]. An epitaxial PLZT films have been deposited on LaAlO₃ (100) substrates by pulse laser deposition due to the close lattice matching and similar perovskite structures [15]. Up to date, BST thin films on Pt-Si substrates with LSCO buffer layers have been few reports, and excellent electrical properties have not been achieved in these structures. In the present study, BST films were prepared on Pt/Ti/SiO₂/Si substrates by pulsed laser deposition (PLD) with and without LSCO buffer layers, respectively. The (100)-oriented BST/LSCO/Pt/Si structures have good dielectric properties, showing a potential application in tunable microwave devices.

2 Experimental

LSCO and BST thin films were deposited by Pulsed laser deposition (PLD) technique. KrF excimer laser radiation ($\lambda = 248$ nm, 650 mJ, 25 ns) was focused on a rotating target set in the chamber through a quartz window. The incident angle of laser beam to the target surface was fixed to be 45°. Substrate were placed parallel to the target surface with a target-substrate distance of 50 mm. Pure oxygen was used as reactive agent during deposition, and was introduced into the chamber through a needle valve. The substrate was heated by radiation from Pt resistive heater with a thermocouple embedded in the heater. Disk-type La_{0.5}Sr_{0.5}CoO₃ (LSCO) and Ba_{0.6}Sr_{0.4}TiO₃ (BST) ceramic targets were prepared by conventional ceramic process using BaCO₃ (99.9% purity), SrCO₃ (99.9% purity), TiO₂ (99.9% purity), La₂O₃ (99.99% purity) and Co₂O₃ (99.99% purity) as starting materials, which mixed the appropriate ratio of precursor oxide powders, pressed the powders into pellets, and sintered them to high density. The LSCO buffer layer about 100 nm was deposited on the Pt/Ti/SiO₂/Si substrate at 600 °C in oxygen pressure of 20 Pa by PLD (a laser fluence of 2.0 J/cm², a repetition rate of 3 Hz). The bottom electrodes were in situ annealed at 600 °C for 30 min in O₂ ambient to improve the crystallinity of the films. 300 nm BST thin films were grown on the Pt/Ti/SiO₂/Si and LSCO/Pt/Ti/SiO₂/Si substrates, respectively. The substrate temperature and the oxygen ambient pressure during the growth of BST films were 650 °C and 25 Pa, respectively. To reduce any oxygen deficiency, the samples were also in situ annealed in 5×10^{-4} Pa oxygen at 700 °C for 1 h, and then cooled down slowly to room temperature. For dielectric measurements, the metal-insulator-metal (MIM) capacitor configuration was fabricated. Pt top electrodes with area of 0.03 mm² were deposited on BST films by direct current sputtering through a shadow mask.

The crystal structure and crystallographic orientations of BST thin films were obtained by X-ray diffraction (XRD) using a BeDe1 Scientific diffractometer (Cu K α radiation). Atomic force microscope (AFM, SPM-300HV, SEIKO) was performed to investigate the morphologies and grain size of the film surface. Capacitance and dielectric loss were measured using an HP 4284 impedance analyzer. The current–voltage characteristic was measured with a HP4155B semiconductor parameter analyzer.

3 Results and discussion

The XRD patterns of BST thin films on Pt electrode with and without LSCO buffer-layer are showed in Fig. 1a and b, respectively. All thin films displayed an entirely perovskite phase without other crystalline phases. Mainly oriented (100) peak with weak (110) peak, corresponding to the (100) preferred orientation, was observed for the BST film deposited on LSCO/Pt in Fig. 1b. Whereas, the BST film deposited on Pt has polycrystalline perovskite morphology with highly (110) preferred orientation, as shown in Fig. 1a. The degree of (100) preferred orientation increased by using a LSCO buffer layer. It indicates that the LSCO buffer-layer affected the texture of BST thin films. XRD results also revealed that the LSCO films were single-phase crystalline and (100) orientation as shown in Fig. 1b. Generally, the growth of the films with preferred orientation was known to relate the lattice matching of the film with substrate and the minimization of the surface energy during the film growth process [16]. LSCO films grow preferentially oriented even on the Pt-Si substrate with large mismatch, the preferred orientation of LSCO films may be due to the lower energy of the (100) surface rather

Fig. 1 XRD patterns of BST thin films deposited on (a) Pt and (b) LSCO/Pt electrode

than lattice matching. The PLD technique can facilitate the fabrication of oriented LSCO films. During pulsed laser deposition, particles have high energy. The stable state phase will easily form with these high-energy particles rather than relatively low-energy particles, which may induce the oriented growth. The (100) BST films are promoted as a consequence of the structural match between LSCO and BST.

All BST thin films were investigated to obtain the morphologies and grains size by AFM observations. The typical surface morphologies of the thin films in the area of $300 \times 300 \text{ nm}^2$ are shown in Fig. 2. Both films show the good uniformity of microstructure concerning the absence of discontinuities (pinholes or microcracks), low surface roughness and small grain size. The BST thin films on LSCO substrates have a smoother surface than that of the films on Pt substrates. At the same time, the average grain size in the BST films on LSCO substrates is determined to approximately 65 nm, and the value is smaller than that of the films on Pt substrates (78 nm). The root-mean-square roughness value is calculated to 13.12 and 9.28 nm for the BST thin films on Pt and LSCO/Pt, respectively. This reveals that LSCO offers an appropriate match structurally with BST. Chen et al. reported that the grain size in the PZT films deposited on the metal oxide electrode is known to be smaller than that of the films on metal electrode [17].

Electrical properties of the BST films are obtained through investigating the capacitors with the configuration of Pt/BST/Pt and Pt/BST/LSCO/Pt. The low-frequency tuning properties of the BST films were measured at 10 kHz with an HP 4284A impedance analyzer. The applied electric field dependence of the dielectric constant for BST films grown on Pt and LSCO/Pt is shown in Fig. 3. The BST film grown on Pt has a maximum dielectric constant of 226, while BST film grown on LSCO/Pt shows a maximum dielectric constant of 1010. The tunability is defined as $(\epsilon_{\max} - \epsilon_{\min})/\epsilon_{\max}$, where $\epsilon_{\max}$ and $\epsilon_{\min}$ are the maximum and minimum measured permittivity. The tunability of the BST films on LSCO was value of 82.4%, while that of BST films on Pt was 36.17% for 330 kV/cm. The dielectric loss of BST films at 10 kHz without and with LSCO buffer layers was about 2.64% and 3.1%, respectively. Note that this value is rather attractive for applications in tunable microwave electronics, such as, in phase shifter devices.

In order to compare films with varied dielectric properties for use in tunable device applications, the figure of merit (FOM) is a frequently used parameter to characterize the correlations between the tunability and the dielectric loss. For BST thin films intended for electronically tuned device applications, the interplay between the dielectric loss and tunability is usually characterized by the figure-of-merit, K , defined as $K = [\text{tunability} / \tan \delta] = [(\Delta C / C_0) / \tan \delta]$. FOM

Fig. 2 AFM images of the surface morphology of BST thin films prepared on (a) Pt and (b) LSCO/Pt electrodes

value reflects the fact that a tunable microwave circuit cannot take full advantage of high tunability if the loss factor is too high. Ideally, the FOM value is desired to be as high as possible. The FOM for the BST thin film on the LSCO bottom electrode was 26.6. These values are relatively higher in comparison with those on the Pt bottom electrode (13.7).

Figure 4 shows the dielectric constant of the BST thin films deposited on both types of the substrates above mentioned at room temperature. The frequency range for

Fig. 3 Dielectric constant characteristics of BST thin films grown on Pt and LSCO/Pt electrodes

these measurements was 20 Hz–100 kHz with oscillation voltage of 0.1 V. The films using Pt/LSCO as bottom electrodes possess a much larger dielectric constant than the films using Pt as bottom electrodes. The dielectric constants for the BST thin film deposited on the LSCO/Pt electrode and Pt substrates measured at 100 kHz were 975 and 124, respectively. The dielectric constant of the BST film grown on LSCO buffer layer is considerably higher than that obtained at the same deposition condition using a Pt electrode. Application of LSCO buffer layer markedly suppresses inter-diffusion between BST and Pt and pronouncedly enhances the formation kinetics of crystalline BST phase. Therefore, LSCO can suppress the formation of a low dielectric layer at BST/LSCO interface. At the same time, it is understood that the dielectric constant of BST thin films can be affected by its crystallization. Hence, the enhanced (100) preferential orientation can result in the increase of dielectric constant of BST thin films.

Fig. 4 Frequency dependence of dielectric constant of BST thin films on Pt and LSCO/Pt electrodes

It was shown that the dielectric constant of the BST thin films directly on Pt electrode decreased drastically with increasing frequency. In contrast, the BST thin films with LSCO buffer layer were almost independent of the frequency. As we know, the frequency dependence of dielectric was attributed to the dielectric relaxation. The BST/Pt contact can lead to a formation of a Schottky junction at the interface. When an oscillation voltage was applied in the dielectric measurement, the depletion layer width was modulated with electrons charging or discharging at oxygen vacancies in the depletion layer. The migration of electrons in this process may result in dielectric relaxation. The result indicates that there were more oxygen vacancies at the Pt/BST interface, which suggested that oxygen atoms in BST thin films were thermodynamically favored by Ti atoms due to the great strength of Ti–O bond. In contrast, there were fewer oxygen vacancies at the LSCO/BST interface, because the chemical and structure similarity between LSCO and BST reduced interfacial oxygen vacancies.

For practical application, the leakage current should be as low as possible. Figure 5 shows a comparison of leakage current density between BST films on Pt and on LSCO/Pt. It is clear that the leakage current density of BST thin films on LSCO buffer-layer is lower than that of BST thin films on Pt electrode. Generally, the interdiffusion between the film and substrate can affect the leakage current of BST thin films. From above analysis, it is considered that the reduction of leakage current density is possibly due to the LSCO buffer-layer acting as a good template for BST thin film, which can reduce grain oxygen vacancies in BST thin film and suppress the dead layer between Pt and BST thin films. When applied voltage is lower 3 V, no enough oxygen vacancies compensate the electron for the BST/LSCO/Pt sample, the

Fig. 5 Bias voltage dependence of leakage current density of Pt/ $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3/\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ and Pt/ $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ /Pt capacitors

leakage current is more than that of BST/Pt sample. With increasing the applied voltage, the leakage current density of the BST film satisfies the SCLC behavior. As BST/LSCO/Pt sample have no low dielectric constant dead layer, the leakage current is lower than that of BST/Pt sample. On the other hand, the decreased leakage current was also found to be dependent on grain size of the film. The BST films with large grain size have short conduction paths along the highly resistive grain boundary, leading to higher leakage current compared with BST film with smaller grain size [18]. The present results show that the buffer LSCO layer plays an important role in the structure and electrical properties of the BST thin films, which is useful in tailoring the orientation, microstructure, and properties of the films for practical applications.

4 Conclusion

In conclusion, we have analyzed the influence of LSCO buffer layer on the microstructure and properties of the BST thin films. The films on LSCO/Pt have smaller grain size and higher dielectric constant than those on Pt/Ti/SiO₂/Si. The tunability of the BST films on LSCO increase significantly from 36.17% to 82.4%, while the figure of merit of the films still increases from 13.7 to 26.6. The obtained results demonstrate that LSCO/Pt can be a suitable bottom electrode for BST thin films in the microwave application.

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