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a-b axis-oriented lanthanum doped $Bi_4Ti_3O_{12}$ thin films grown on a TiO_2 buffer layer

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a-b axis-oriented, lanthanum doped $Bi_4Ti_3O_{12}$ (BLT) thin films with a TiO_2 rutile buffer layer deposited on $Pt/Ti/SiO_2/Si$ substrates were grown by the soft chemical method. Butterfly dielectric behavior has been achieved and can be ascribed to the ferroelectric domain switching. The remanent polarization and the coercive voltage for the film deposited on TiO_2 buffer layer were 22.2 $\mu C/cm^2$ and 1.8 V, respectively. Random-oriented BLT films showed a reduction in switching polarization when compared to the *a-b* axis-oriented films. Due to the excellent physical properties, these films are a promising candidate for use in lead-free applications in ferroelectric devices. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2356096]

INTRODUCTION

Ferroelectric thin films have been extensively studied for their applications for nonvolatile random access memory (NvRAM) and high-speed random access memories.[1–3] As a fatigue-free material, $Bi_{4-x}La_xTi_3O_{12}$ films ($x=0.75$, BLT75) is of particular interest because it can be crystallized at relatively low processing temperatures (close to 650 °C), making it more compatible with Si-based integrated circuit (IC) technology. The $Bi_{14}Ti_{13}O_{12}$ (BIT) has a spontaneous polarization in the *a-c* plane at an angle of approximately 4.5° to the *a* axis, and exhibits two independently reversible components along the *c* and *a* axes.[4–7] It shows coercive fields (E_c) of 3.5 and 50 kV/cm and remanent polarization (P_r) values of 4.0 and 50 $\mu C/cm^2$ along the *c* and *a* axes, respectively. The large P_r of the *a* axis takes advantage of the reduction of the memory cell area of nonvolatile ferroelectric random access memory (Nv-FeRAM). The mechanism of *a* and *b* axis orientations of the thin film with the TiO_2 buffer layer is supposed to be caused by the interval of oxygen ion distribution along (101) of the TiO_2 rutile, which is closer to the *a* and *b* axis lattice parameters (0.541 nm) than that to the *c* axis parameter (3.283 nm) of BIT. The concept of lattice mismatch cannot explain the *a* and *b* axis orientations of the BIT thin films since it is estimated to be approximately 5.4%, which is almost of the same order as the lattice mismatch between BIT and Pt. In the present study, a TiO_2 rutile buffer layer was prepared on a (111)-oriented $Pt/Ti/SiO_2/Si$ substrate by the soft chemical method and microwave annealing.[8]

The (111)-oriented Pt layer is most commonly stacked as an electrode between the ferroelectric and the insulator layer because of its chemical and thermal stabilities at high temperatures. Therefore, the TiO_2 rutile could be a promising buffer layer, which can avoid the interdiffusion between the ferroelectric phase and the Pt substrate. Thus, we demonstrate in this paper that the TiO_2 rutile buffer layer is very effective.

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EXPERIMENT

Titanium isopropoxide (Aldrich), bismuth nitrate (Aldrich), and lanthanum carbonate (Merck) were used as raw materials. The three different precursor solutions containing either lanthanum, bismuth, or titanium were prepared by adding the raw materials to ethylene glycol and concentrate aqueous citric acid under heating and stirring. The molar ratio of metal:citric acid:ethylene glycol was always 1:4:16. Appropriate quantities of La, Ti, and Bi solutions were then mixed and homogeneized by stirring at 90 °C. The viscosity of the resulting solution was adjusted to 20 cP by controlling the water content using a Brookfield viscosimeter. The TiO_2 buffer layer was deposited on (111) $Pt/Ti/SiO_2/Si$ substrates by the soft chemical method and microwave annealed at 500 °C for 10 min. The previously prepared Ti precursor solution (with viscosity of 20 cP) was used as the Ti source for the buffer layer. BLT thin films were spin coated on $TiO_2/Pt/Ti/SiO_2/Si$ and $Pt/Ti/SiO_2/Si$ substrates by a commercial spinner operating at 5000 rpm for 30 s (spin coater KW-4B, Chemat Technology). In this work, an excess of 5 wt % of Bi (related to the stoichiometric bismuth mass in the mixture) was added to the solution aiming to minimize the bismuth loss during the thermal treatment. BLT thin films were annealed at 700 °C for 2 h in a conventional furnace. Through this process, we have obtained thickness values of about 400 nm for the ferroelectric film, reached by repeating the spin-coating and heating treatment cycles. Phase analysis was performed at room temperature by x-ray diffraction (XRD) in Bragg-Brentano geometry (Rigaku 2000) at Cu $K\alpha$ radiation. Furthemore, topography and thickness were examined using atomic force microscopy (AFM) (Digital Instruments, Nanoscope IV) and scanning electron microscopy (Topcom SM-300), respectively. The upper electrodes of Au for the electrical measurements were prepared by evaporation through a shadow mask with 0.2 mm^2 dot area. Dielectric and ferroelectric properties of the capacitor were measured with an HP4192A impedance/gain phase analyzer and a Radiant Technology RT6000 A in a virtual ground mode, respectively.

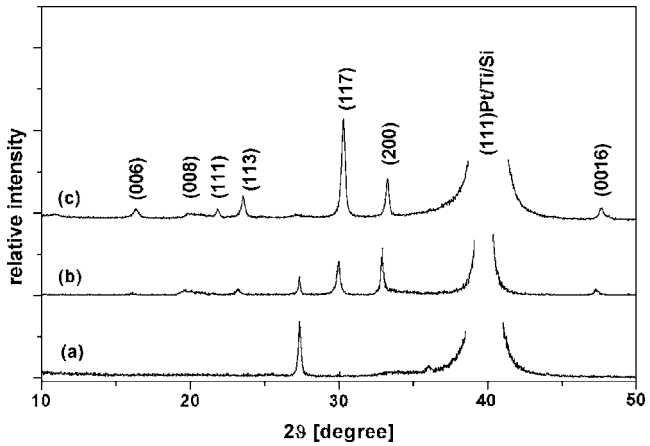

FIG. 1. X ray diffraction for (a) TiO_2 buffer layer on $Pt/Ti/SiO_2/Si$, (b) BLT75 on $TiO_2/Pt/Ti/SiO_2/Si$, and (c) BLT75 on $Pt/Ti/SiO_2/Si$ substrate.

RESULTS AND DISCUSSION

It is well known that bismuth layered ferroelectrics are strongly anisotropic in nature.[9] The ferroelectric properties of bismuth layered thin films are mostly influenced by the orientation of the film. Figure 1 shows the XRD pattern of the as-deposited BLT75 thin films with the rutile buffer layer, with no buffer layer and the TiO_2 peak deposited on platinum coated silicon substrates. The film thickness of the TiO_2 buffer layer was approximately 50 nm.

A sharp peak at $2\theta=40°$ is the Pt (111) peak. A weak peak at $2\theta=27.4°$ corresponds to the TiO_2 rutile (110) peak. The film thicknesses were also approximately 400 nm. No secondary phases were observed in these XRD patterns. The BLT75 thin film with no buffer layer exhibits a random-oriented single phase. In contrast, the XRD pattern of the BLT thin film with TiO_2 rutile buffer layer exhibits highly *a* and *b* axis-oriented BLT single phase. This may indicate that the TiO_2 rutile buffer layer does not act as simple barrier layer only, which can avoid the interdiffusion between the BLT thin film and the Pt substrate.

AFM images revealed that the surface of the BLT75 film with no buffer layer (Fig. 2) exhibits platelike grains while the surface of the film with buffer layer possesses rounded grains (Fig. 3). The films crystallized on platinum substrates are random oriented and present less energetic favorable form (elongated grains) with a typical bismuth layer perovskite structure. Meanwhile, the films crystallized on the rutile phase are oriented and the grains tend to assume the more energetic favorable form (rounded).

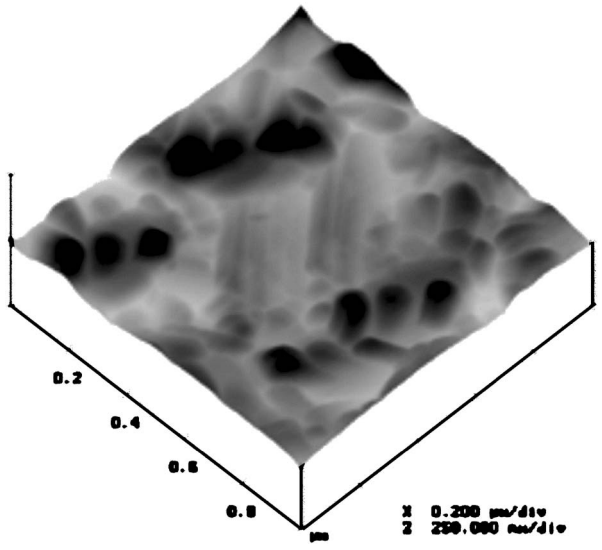

FIG. 2. AFM image for BLT75 thin film on $Pt/Ti/SiO_2/Si$ substrate.

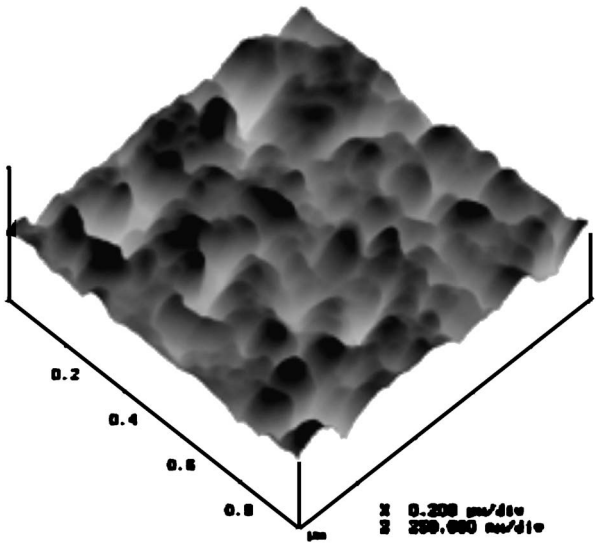

FIG. 3. AFM image for BLT75 thin film on $TiO_2/Pt/Ti/SiO_2/Si$ substrate.

Figure 4 shows the hysteresis loop for the BLT75 thin films with and without buffer layer. Both hysteresis loops exhibit a good shape and saturation was observed. The remanent polarizations of the films with and without TiO_2 layer were $P_r=22.2$ and 20.3 $\mu C/cm^2$, respectively, i.e., the titanium oxide layer does not change the remanent polarization significantly. This means that both, a random orientation (no buffer layer) and the preferred *a* and *b* axis orientations lead to a high remanent polarization. However, due to the different orientations of the films, this changes when examining the corresponding coercive fields E_c, which were 116 and 150 kV/cm, respectively. Due to the anisotropic characteristics, the dielectric properties of bismuth layered thin films are often influenced by the crystal structure and orientation, which defines the magnitude of switchable domains that con-

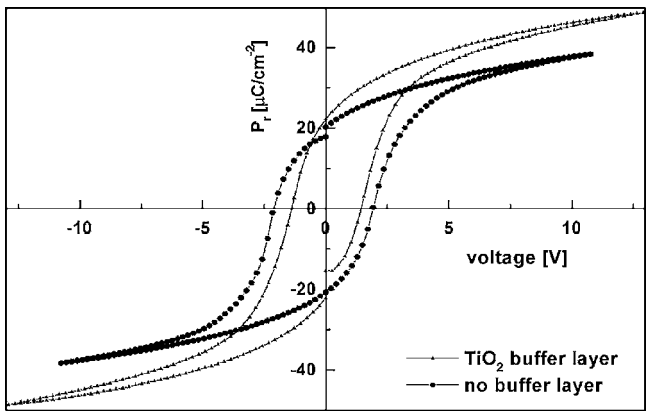

FIG. 4. Hysteresis loops for BLT75 thin films deposited on $Pt/Ti/SiO_2/Si$ substrate with and without titanium oxide buffer layer.

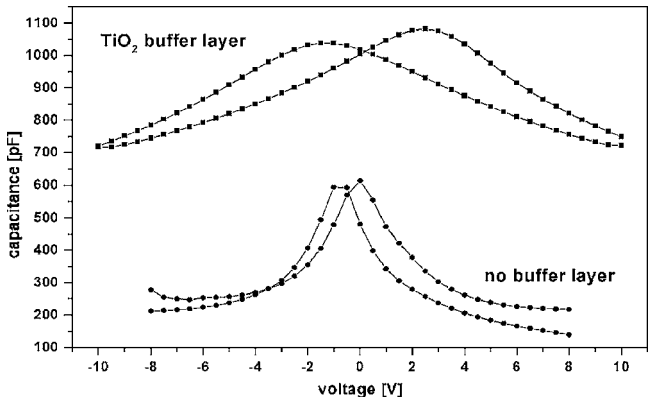

FIG. 5. Capacitance-voltage characteristics for BLT75 thin films deposited on $Pt/Ti/SiO_2/Si$ substrate with and without titanium oxide buffer layer.

tribute to the dielectric displacement. The *C-V* characteristics are shown in Fig. 5. The butterfly-shape curves that characterize every ferroelectric material are consistent with the other electrical measurements and the microstructural data. Both curves are symmetric around the zero bias axes, indicating that the films contain few movable ions or charge accumulation at the film-electrode interface. The measured value of relative permittivity at a frequency of 100 kHz is 190 for the films deposited on $Pt/Ti/SiO_2/Si$ substrates and 300 when a titanium oxide buffer layer was used. This higher dielectric constant can be correlated with the increased grain size, which was found by AFM for the film with buffer layer. The main difference in the coercitive field of *P-E* and *C-V* curves originated from the setup measurements once they performed at different frequencies where the domain alignment is a time dependent process and plays an important role in the switching behavior of the domains. Therefore, the sweep voltage ranges differ greatly and, consequently, also the (dV/dt) voltage sweep per time unit leading to different domain alignment kinectics.

Figure 6 shows the trend in leakage current density (J) with the application of electric voltage. The leakage current

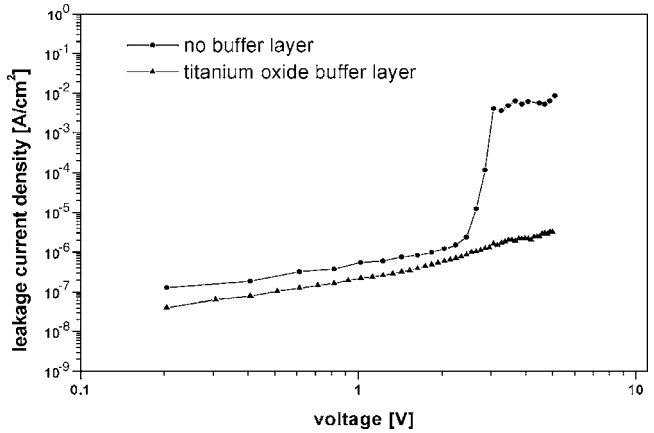

FIG. 6. Dependence of leakage current density on voltage for BLT75 thin films deposited with and without titanium oxide buffer layer.

density of the ferroelectric film is only slightly reduced by the insertion of the rutile buffer layer. This indicates that the role of TiO_2 is to decrease the nucleation probability, to favor the growth of *a-b* axis oriented films, and not to consume the oxygen vacancies by changing their oxygen nonstoichiometry. Thus, the buffer layer does not prevent a possible small accumulation of oxygen vacancies near the interface. It does, however, provide films with larger grain sizes due to a reduced nucleation rate. At low fields the leakage current density increases linearly with the applied field according to an Ohmic characteristic. At higher fields, these films exhibit nonlinear *J-V* relationships. The leakage density at 1.0 V was about 10^{-7} A/cm^2. This value is relatively reasonable for application in memories once a high leakage current generally leads to some loss of the stored data written in a cell and, thus, requires a frequent refresh and a high power consumption. It has been estimated that the upper limit of the allowable leakage current density for a 200 nm thick film[10] is 3 mA/cm^2. The leakage current can only be measured in the presented range here. A voltage of 10 V applied across a sample destroys the film.

CONCLUSIONS

In conclusion, we have successfully prepared *a* and *b* axis-oriented BLT75 thin films with the TiO_2 rutile buffer layer deposited on $Pt/Ti/SiO_2/Si$ substrates using the soft chemical method. Such BLT75 thin films exhibit pronounced *a* and *b* axis orientations. The morphology of BLT75 thin films is improved by the TiO_2 rutile buffer layer. The films show relatively large P_r values and a high dielectric constant, which originates from *a* and *b* axis orientations. These excellent ferroelectric and structural properties are favored by the rutile buffer layer, which reduces the initial nucleation rate when crystallizing the BLT75 thin film. Finally, we would like to propose TiO_2 rutile as a promising buffer layer for the deposition of *a-b* axis-oriented BLT75 thin films.

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