Fatigue-free behavior of highly oriented $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films grown on $Pt/Ti/SiO_2/Si(100)$ by metalorganic solution decomposition

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(Received 22 August 2000; accepted for publication 23 October 2000)

Fatigue-free and highly *c*-axis oriented $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) thin films were grown on $Pt/Ti/SiO_2/Si(100)$ substrates using metalorganic solution decomposition. Films annealed above 500 °C were characterized by strong *c*-axis preferential growth with an in-plane alignment of grains. The BLT film capacitors with a Pt top electrode showed excellent ferroelectric properties. The remanent polarization $(2P_r)$ and the coercive field (E_c) were in the range of 26–28 $\mu C/cm^2$ and 50–75 kV/cm, respectively. More importantly, the BLT capacitors did not show any significant fatigue up to 3.5×10^{10} read/write switching cycles at a frequency of 1 MHz. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1333686]

There has been extensive research on ferroelectric (FE) thin films for nonvolatile memory device applications.[1–5] Perovskite ferroelectrics, especially lead zirconate titanate $[PbZr_xTi_{1-x}O_3$ (PZT)], represent an important class of FE materials. PZT capacitors with simple metal (such as Pt) electrodes in general show excellent piezoelectric/ferroelectric properties and are compatible with Si-based integrated circuit (IC) technology. However, their fatigue resistance is poor and degrades seriously after being subjected to $10^7–10^8$ switching cycles.[6,7] Although the fatigue problem in PZT films can be solved by using metaloxide electrodes, these electrodes are difficult to prepare and increase leakage currents. Some layered perovskites such as strontium bismuth tantalate $(SrBi_2Ta_2O_9)$ and lanthanum substituted bismuth titanate $[Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT)] show superior fatigue resistance compared to Pt/PZT/Pt capacitors.[8,9] As a fatigue-free material, BLT is of particular interest because it can be crystallized at low processing temperatures below 650 °C, which is compatible with Si-based IC technology.

Recently, fatigue-free BLT films have been grown on $Pt/Ti/SiO_2/Si(100)$ substrates using pulsed laser deposition (PLD).[9] However, the BLT films prepared by the PLD method were characterized by a mixed orientation of grains. As pointed out by Kingon,[10] mixed orientation increases bit-to-bit variability capacitors for high-density ferroelectric memory devices. In addition, the PLD-grown films generally exhibit wide variation in the film thickness. These are problematic for device applications since a large-scale process in the IC industry requires a uniform and homogeneous film over a large area of silicon substrate for the reproducibility of devices. The metalorganic solution decomposition (MOSD) employed in this study, however, fulfills these requirements as it offers excellent uniformity over a large area, easy composition control, short fabrication time as well as low-temperature process at a comparatively low cost. In this letter, we report on the ferroelectric property and fatigue-free behavior of BLT films prepared by the MOSD method. Unlike BLT films fabricated by the PLD method, the present BLT films were characterized by a high *c*-axis oriented growth with a homogeneous in-plane orientation.

The BLT films were prepared on $Pt/Ti/SiO_2/Si(100)$ substrates using a repeated coating/dying cycle. The precursor solution for the coating was prepared by dissolving appropriate amounts of bismuth acetate $[Bi(CH_3COO)_3]$, lanthanum acetate hydrate $[La(CH_3COO)_3 2H_2O]$, and titanium isopropoxide $\{Ti[(CH_3)_2CHO]_4\}$ in acetic acid at room temperature. Details of the sol preparation and coating are described elsewhere.[11] The dried films were amorphous as determined by x-ray diffraction (XRD), and were subsequently crystallized by thermal annealing for 1 h in air at various temperatures ranging between 400 and 650 °C.

As-annealed films were specular, crack-free, uniform, dense, and adhered well on the substrates used. The films also showed very smooth surfaces, as observed using an optical microscope. Microstructural examination using a field-emission scanning electron microscope (FE–SEM) showed only fine-sized grains in the films. The film thickness was estimated using both surface profilometry and cross-sectional FE–SEM. Chemical compositions of the BLT films were determined using energy dispersive x-ray and electron microprobe techniques. The stoichiometry of the BLT film annealed at 650 °C was Bi:La:Ti = 3.25:0.75:3.

For the fabrication of BLT capacitors, Pt top electrodes were deposited using the electron-beam evaporation method. A typical area of the top electrodes was 10^{-4} cm^2. Electrical measurements were performed on the BLT capacitors using an RT6000S tester equipped with a micrometer probe station.

The crystallization and the preferential growth of the annealed films were examined using XRD measurements. Figure 1 shows the XRD θ–2θ scan results of the BLT films annealed at various indicated temperatures for 1 h. For the film annealed at 400 °C, diffraction peaks that correspond to

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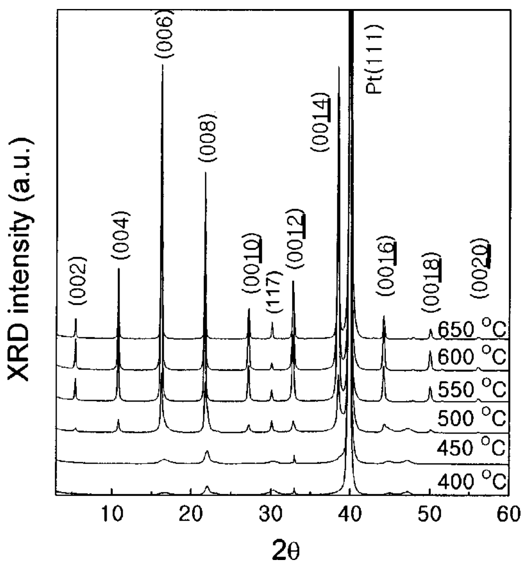

FIG. 1. XRD patterns of BLT films grown on $Pt/Ti/SiO_2/Si(100)$ substrates. The films were thermally annealed for 1 h at various temperatures ranging between 400 and 650 °C.

(008) and (117) reflections were observed. This indicates that the onset of crystallization to a layered perovskite is near 400 °C. The most prominent feature of the XRD patterns presented in Fig. 1 is that the BLT film annealed above 550 °C shows a high *c*-axis oriented preferential growth with only a minor fraction of (117) orientation. The degree of $(00l)$-type preferential growth, as estimated using Lotgering's orientation factor,[12] is 99% for the BLT film annealed at 550 °C while it decreases slightly and is 96% for the film annealed at 650 °C.

The degree of the in-plane alignment of grains in the films was further examined using the XRD pole-figure analysis. Since the BLT crystal with a *c*-axis orientation possesses a four-fold symmetry, four poles should appear in the pole figure if the *a* and *b* axis of grains in the film are well aligned. As demonstrated in Fig. 2(a), the pole figure obtained from the film annealed at 650 °C only exhibits the four poles separated one from another by 90°. The 90° rotational symmetry clearly indicates that the BLT film has a homogeneous in-plane alignment of grains on the $PT/Ti/SiO_2/Si(100)$ substrate. Until now, the growth of a highly *c*-axis oriented BLT film on a $PT/Ti/SiO_2/Si(100)$ substrate with a homogeneous in-plane orientation has not been reported elsewhere. In addition, the angle between $(00l)$ plane and (117) plane, as estimated from the pole figure, was $54° \pm 2°$. This value is close to the theoretical value of 51°, as evaluated based upon the lattice structure of bismuth titanate $[Bi_4Ti_3O_{12}$ (BT)], and to the reported value of 56° for the BT film grown on the $Al_2O_3(0001)$ substrate.[13] As shown in Fig. 2(b), the XRD rocking curve of the (006) peak shows the full width at half maximum of 1.3°. This value is significantly lower than the reported value of 2.8° for the BT film on a Pt substrate.[14]

Figure 3 shows hysteresis loops of a BLT capacitor measured at various applied voltages ranging between 3 and 10 V. The film was annealed at 650 °C for 1 h, and its thickness was 250 nm. As presented in Fig. 3, the BLT capacitor is characterized by well-saturated polarization-electric field $(P-E)$ switching curves. The remanent polarization $(2P_r)$ of the capacitor is 27 ± 1 $\mu C/cm^2$ at an applied voltage of 10 V. This value is significantly higher than that of 8.3 $\mu C/cm^2$ for $SrBi_2Ta_2O_9$, another fatigue-free FE material.[15] The present $2P_r$ value is even higher than the value of 24 $\mu C/cm^2$ for the PLD-grown BLT films reported by Park *et al.*[9] The coercive field (E_c) of the BLT capacitor is in the range of 50–75 kV/cm, which is comparable to the previously reported value of 50 kV/cm for the PLD-grown capacitor.[9] More importantly, these values, i.e., P_r and E_c, of the capacitor (with an electrode area of 10^{-4} cm^2) are constant throughout the whole area of the film, which presumably results from the homogeneity of the grain orientation in the present MOSD-derived film. These features in the ferroelectric properties can possibly remove the problems as-

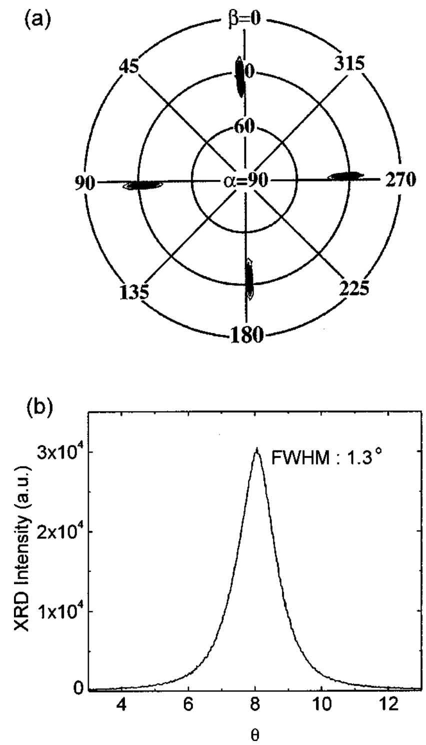

FIG. 2. The pole figure and the rocking curve of the BLT film thermally annealed at 650 °C for 1 h: (a) the XRD pole figure for the (117) reflection, and (b) the rocking curve for (006) plane.

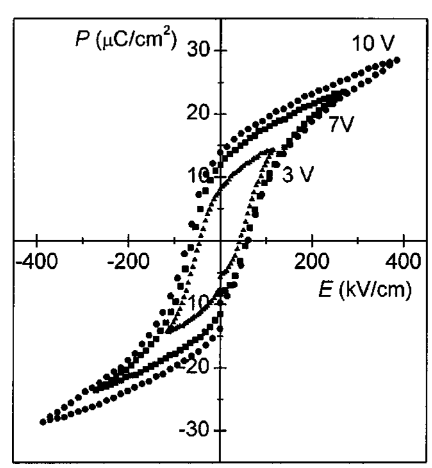

FIG. 3. $P-E$ hysteresis loops for the BLT film on a $Pt/Ti/SiO_2/Si(100)$ substrate at three different applied voltages. The film was thermally annealed at 650 °C for 1 h. The size of the Pt top electrode was 10^{-4} cm^2.

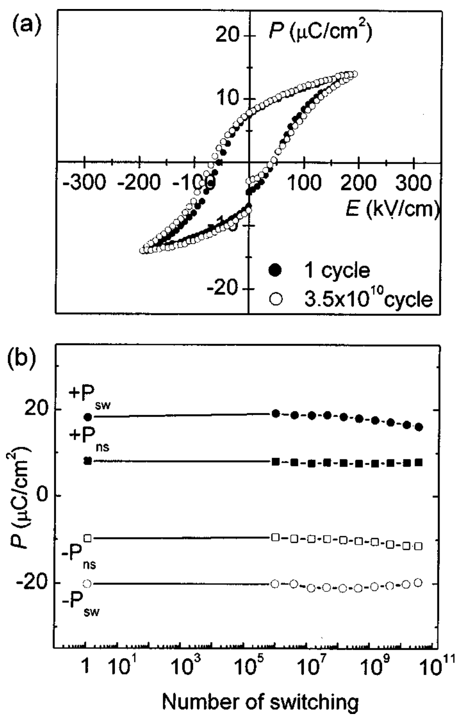

FIG. 4. Electrical fatigue characteristics of the BLT capacitors before and after being subjected to 3.5×10^{10} read/write cycles at a frequency of 1 MHz: (a) $P-E$ hysteresis loops measured at an applied voltage of 5 V before and after the switching cycle, and (b) fatigue test results determined using a fatigue voltage of 3 V and a measuring voltage of 5 V at a frequency of 1 MHz.

sociated with the bit-to-bit variability in film capacitors and will significantly enhance the potential value of the BLT films for the ferroelectric random access memory (FRAM) device applications.

The fatigue characteristics of the BLT capacitor are summarized in Fig. 4. The film showed little change both in the switching polarization (P_{sw}) and in the nonswitching polarization (P_{ns}) up to 3.5×10^{10} switching cycles. The $P-E$ curves were obtained at an applied voltage of 5 V before and after the electrical fatigue test using a fatigue voltage of 3 V. The values of $2P_r$ and E_c before the fatigue test were 14.3 μC/cm^2 and 50 kV/cm, respectively, at an applied voltage of 5 V. After being subjected to 3.5×10^{10} cycles, these were still retained at 15.4 μC/cm^2 and 52 kV/cm for the same applied voltage. Furthermore, no significant change in the shape of the hysteresis loops was observed even after being subjected to 3.5×10^{10} read/write cycles at a frequency of 1 MHz.

In conclusion, the fatigue-free $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) thin films characterized by a strong c-axis preferential growth with a homogeneous in-plane orientation were grown on Pt/Ti/SiO_2/Si(100) substrates at 650 °C using the MOSD method. The BLT capacitors fabricated using a Pt top electrode showed well-saturated $P-E$ curves with a remanent polarization of 27 ± 1 μC/cm^2 at an applied voltage of 10 V. More importantly, the BLT capacitors did not show any significant fatigue up to 3.5×10^{10} read/write switching cycles at a frequency of 1 MHz.

This research was financially supported by the Korea Institute of Science and Technology Evaluation and Planning (KISTEP) through the National Research Laboratories (NRL) Program, and by POSTECH through the BSRI Special Fund-2000.

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