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Retention characteristics in $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ thin films prepared by the polymeric precursor method

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Ferroelectric $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLT) thin films were deposited on Pt/Ti/SiO₂/Si substrates by the polymeric precursor method. The films present *c*-axis preferred orientation after annealing at 700 °C for 2 h in conventional furnace. All the capacitors showed good polarization fatigue characteristics at least up to 1×10^{10} bipolar pulse cycles and excellent retention properties up to 1×10^4 s. We found that the polarization loss is insignificant with five write/read voltages at a waiting time of 10 000 S. Independently of the applied electric field the retained switchable polarization approached a nearly steady-state value after a retention time of 10 s. © 2005 American Institute of Physics. [DOI: 10.1063/1.1886893]

Ferroelectric materials have attracted much attention due to their potential use for nonvolatile memory devices, such as ferroelectric random access memory (FRAM). There have been many reports on the electrical properties of candidate materials, such as $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) and $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ (PZT).¹ One property required for ferroelectric memories is long term stability. The application of ferroelectric thin films to the microelectronic industry is currently limited by the degradation of the polarization state. Device reliability, including factors such as fatigue, imprint and retention, have constituted the main obstacle to commercialization of FRAM devices. Recently, ferroelectric $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLT) was found to be a new candidate material for FRAM applications due to its high resistance to fatigue and low processing temperature.² However, the retention characteristics of BLT films have so far not been reported by the polymeric precursor method. In a memory element, a data bit (1 or 0) should be stored and made available for query at some later time. Retention is the ability of a memory element to maintain a given data state as time elapses. In most retention studies, ferroelectric capacitors exhibited a significant loss in retained polarization within the first 1 s after writing and then a relatively slight decay thereafter.^{3–7} Retention loss causes a reduction in the difference between switched (P^*) and non-switched (P^-) polarizations, i.e., $\Delta P = (P^*) - (P^-)$ and leads to an inability to distinguish between the two logic states. Therefore, it is quite important to have good retention properties for any ferroelectric material to be utilized for FRAM applications. In this letter, we report systematic studies on the retention characteristics of BLT thin films obtained by the polymeric precursor method. We have also investigated the influence of the applied electric field on the retention properties of the BLT thin films. The BLT thin films were prepared by the polymeric precursor method, as described elsewhere.^{8,9} The BLT thin films were spin coated on Pt/Ti/SiO₂/Si substrates by a commercial spinner operating at 5000 revolutions/min for 30 s (spin coater KW-4B, Che-

mat Technology). In this work, an excess of 5% wt of Bi was added to the solution aiming to minimize the bismuth loss during the thermal treatment. Without this additional bismuth the pure phase could not be obtained as was reported in literature.¹⁰ The thin films were annealed at 700 °C for 2 h in the conventional furnace. Through this process, we have obtained thickness values of about 400 nm for BLT, reached by repeating the spin coating and heating treatment cycles. The thickness of the annealed films was studied using scanning electron microscopy (Topcom SM-300) by looking at the transversal section. In this case back scattering electrons were used. Phase analysis of the films was performed at room temperature by x-ray diffraction (XRD) using a Bragg–Brentano diffractometer (Rigaku 2000) and Cu $K\alpha$ radiation. The morphology of the thin films were examined using atomic force microscopy (AFM) (Digital Instruments, Nanoscope IIIa). A 0.5 mm diameter top Au electrode for the electrical measurements were prepared by evaporation through a shadow mask at room temperature. The electric properties were measured by an Au/BLT/Pt/Ti/SiO₂/Si (100) capacitor structure. Ferroelectric properties of the capacitor were measured on a Radiant Technology RT6000 A tester equipped with a micrometer probe station in a virtual ground mode. For the fatigue measurements, internally generated 8.6 μs wide square pulses or externally generated square pulses were used. The retention characteristics of the films were measured by observing the time-dependent changes of P^* and P^- independently. For P^* , the capacitor was switched with a negative write pulse and read by a positive read pulse after retention time t . For P^- , positive pulses were used for both writing and reading.

Figure 1 presents the XRD of $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLT) thin films deposited on Pt/Ti/SiO₂/Si substrates by a chemical-soft method. Only peaks of the main phase were detected suggesting that substitution of Bi by La does not lead to formation of secondary phases. The split of the (0010) and (200) peaks into two duplets indicates the change of crystal structure from the orthorhombic to the tetragonal

FIG. 1. X-ray diffraction of $\text{Bi}_{1-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ films ($x=0.75$) deposited on Pt/Ti/SiO₂/Si substrates at 700 °C for 2 h by the soft chemical method. Inset of AFM image obtained in the contact mode for $\text{Bi}_{1-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ films ($x=0.75$) deposited on Pt/Ti/SiO₂/Si substrates at 700 °C for 2 h by the soft chemical method.

system. Besides the BLT peaks, the characteristic peak for (111) platinum coated silicon substrates at $2\theta=40^\circ$ was identified. It can be observed that the addition of lanthanum ($x=0.75$) results in a c -axis preferred orientation. Such a well-developed c orientation in the La-doped films was also reported by other methods.^{11,12} The inset in Fig. 1 shows the AFM surface morphology obtained in the contact mode of the film deposited on Pt/Ti/SiO₂/Si substrate. A homogeneous surface, smooth and crack free was observed indicating that the chemical soft method allows the preparation of films with controlled morphology. The surface morphology of the BLT films shows grains in the form of platelets, as expected from the preference for the c orientation observed in XRD. The grains are evenly distributed with an average grain size of 140 nm and surface roughness equal to 8.0 nm.

Figure 2 shows the hysteresis loops acquired before and after waiting time of 10 000 s with 5 V write/read voltages, respectively. The switchable polarization exhibits almost no loss with 5 V write/read voltage after 10 000 s retention time. This suggests that there no pinning of domain walls in BLT thin film at 5 V write/read voltage. Similar results were observed for SBT thin films deposited on platinum coated silicon substrates where the switchable polarization present no loss with 9 V write/read voltage, while it exhibited polarization loss with 3 V write/read voltage after a waiting period of 30 000 s.¹³ Ferroelectricity of the lanthanum doped bismuth titanate thin films was observed with remanent po-

FIG. 2. P - E hysteresis loops before and after 10 000 S waiting time for $\text{Bi}_{1-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ films ($x=0.75$) deposited on Pt/Ti/SiO₂/Si substrates at 700 °C for 2 h by the soft chemical method.

FIG. 3. Fatigue as a function of polarization cycles for $\text{Bi}_{1-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ films ($x=0.75$) deposited on Pt/Ti/SiO₂/Si substrates at 700 °C for 2 h.

larization of 21 $\mu\text{C}/\text{cm}^2$ and coercive field 44 kV/cm. The remanent polarization of the BLT film obtained by the soft chemical method is larger than those of other reported in the literature.^{2,14}

When a ferroelectric material is repeatedly cycled from one polarization state to another, its dielectric and ferroelectric properties are observed to change. This phenomenon, known as ferroelectric fatigue, is a limiting factor for the performance of the ferroelectric random access memory (FRAM) devices. The fatigue endurance of BLT thin films were tested at 1 MHz as a function of switching cycles by applying 8.6 μs wide bipolar pulses with maximum amplitudes of ± 5 V. (Fig. 3). P^* is the switched polarization between two opposite polarity pulses and $P^\wedge$ is the non-switched polarization between the same two polarity pulses. The $P^* - P^\wedge$ or $-P^* - (-P^\wedge)$ denote the switchable polarization, which is an important variable for nonvolatile memory application. Fatigue resistance was observed up to 1×10^{10} cycles suggesting that BLT has good potential for applications in memories. The substitution of La for Bi can change the chemical environment of the perovskite layers and solve the fatigue problem of pure BIT thin films. Since a La^{3+} ion has no outer electron, in contrast to a Bi^{3+} ion, which has a lone pair of 6s electrons, less hybridization with O 2p should lead to less structural distortion favoring the improvement of its ferroelectric properties.¹⁵

Retention, which is the time dependent change of the polarization state of the ferroelectric film, is another factor which limits the life of a ferroelectric memory device. Ferroelectric retention properties were measured at room temperature using a Radiant Technology RT6000 A test system (Fig. 4). The test pulse sequence used for retention measurement is as follows: At first, a triangular pulse of -5 V was applied to write a known logic state, then, after a predetermined time, the logic state was sequentially read by applying two triangular pulses of $+5$ V and -5 V. The pulse width for all triangular pulses is 1.0 ms. Time delay between the right pulse and the first read pulse is called the retention time. The capacitor poled with a negative voltage pulse corresponds to the binary digit "1." Similarly the state "0" was written by poling the capacitor by applying a positive pulse and read after a predetermined time interval t with a positive pulse. Figure 4(a) shows the retention characteristics of the BLT films, where the retained switchable polarization $\Delta P = (P^*) - (P^\wedge)$ was plotted as a function of retention time from 1 to 1×10^4 s at various applied electric fields from

FIG. 4. (a) Retention time dependence of the retained polarization of the BLT film with various applied electric fields (75–300 kV/cm) and (b) P^* and P^- of the BLT film for retention time up to 1×10^4 s and applied electric field of 150 kV/cm.

75 to 300 kV/cm. The value of initial polarization decayed and approached a nearly steady-state value after a retention time of 10 s. The corresponding hysteresis loops obtained after the retention test was also essentially identical to that observed before the retention test, indicating that the switchable polarization has almost no loss and the structures have little or no tendency to imprint after 1×10^4 s. The small decay of the retained charge in BLT thin films even after about 1×10^4 s is a favorable indication for memory applications. The long-time retention characteristics of the BLT films are shown in Fig. 4(b). The overall retention time dependence of polarization retention for the BLT film is quite good. After a retention time of 1×10^4 s, the polarization loss was only about 6% of the value measured at $t=1$ s for an applied electric field of 150 kV/cm. Depolarization fields generated by the redistribution of space charge, defects and dipole charges could be the mechanisms for the polarization decay after writing. For the infant period (within 10 s), depolarization fields could be the main contribution to polarization loss. The depolarization field increases with increasing the retained polarization and is time dependent. The long-time retention loss is attributed to the effects of redistribution of defect charges. This effect leads to a small decrease in the polarization by compensating the polarization charges when the redistribution of defect charges is driven by polarization.¹⁶ Due to the dielectric relaxation, the retained charge is generally less than the switched charge measured from the P – E hysteresis loop and the difference between them should be small as possible to maintain enough margin

between the digits “1” and “0.” Retention, like fatigue, is also dependent on the thickness of the film, nature of the electrodes, microstructure of the film, temperature, and the details of the test conditions. The understanding and improvement of the degradation behavior of ferroelectric thin films will have an essential impact on the future success of these films for device applications. Detailed fatigue and retention measurements in close correlation with process conditions are being done to evaluate the merits of lanthanum bismuth titanate thin films for memory applications. In conclusion, c -axis preferred orientation BLT thin films were obtained on Pt/TiO₂/SiO₂/Si substrates by using the soft chemical method through the spin coating technique. High fatigue resistance was observed which proves that our films possess enough quality to be used in nonvolatile random access memories. The polarization retention characteristics of ferroelectric BLT thin films deposited on Pt/TiO₂/SiO₂/Si substrates by the soft chemical method have been investigated. The retention failure tests showed that the BLT films have quite good long-time retention characteristics, retaining 94% of the values measured at $t=1 \times 10^4$ s for an applied electric field of 150 kV/cm. Polarization charge compensation by the redistribution of defect charges should be considered to explain the retention loss in lanthanum doped bismuth titanate thin films for memory applications. The results of these studies are very promising and suggest that BLT thin films are attractive for use as storage element in nonvolatile ferroelectric random access memories.

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