

Control of retention and fatigue-free characteristics in $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ thin films prepared by chemical method

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Received 8 February 2006; received in revised form 4 April 2006; accepted 9 April 2006

Available online 3 May 2006

Abstract

Ferroelectric $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ (CBTi144) thin films were deposited on Pt/Ti/SiO₂/Si substrates by the polymeric precursor method. The films present a single phase of layered-structured perovskite with polar axis orientation after annealing at 700 °C for 2 h in static air and oxygen atmosphere. The *a/b*-axis orientation of the ferroelectric film is considered to be associated with the preferred orientation of the Pt bottom electrode. It is noted that the films annealed in static air showed good polarization fatigue characteristics at least up to 10¹⁰ bipolar pulse cycles and excellent retention properties up to 10⁴ s. On the other hand, oxygen atmosphere seems to be crucial in the decrease of both, fatigue and retention characteristics of the capacitors. Independently of the applied electric field, the retained switchable polarization approached a nearly steady-state value after a retention time of 10 s.

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Keywords: Thin films; Chemical synthesis; Ferroelectricity

1. Introduction

Recently, more and more efforts have been made to develop nontoxic lead-free piezoelectric materials. Bismuth-layered ferroelectrics are considered to be candidate materials for nonvolatile random access memory (NVRAM) application due to their low coercive field and leakage current, long retention, minimal tendency to imprint and little fatigue with usual platinum electrodes [1,2]. The bismuth-layered perovskite is a member of the Aurivillius family, $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$, in which A represents mono-, di-, or tri-valent ions and B represents tetra-, penta- or hexa-valent ions. Compounds such as $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$, $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ and $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$, which have the *n* value of 4, have already been studied for their anisotropic ferroelectricity [3]. CBTi144 is characterized by its high Curie point of about 790 °C and therefore is expected to be useful for special applications at relatively high temperatures [4]. Compounds in that family have anisotropic

ferroelectricity, which is strongly associated with the crystal structure, especially the compounds with *n* equal to an even number which have no polarization along the *c*-axis because there is a mirror plane perpendicular to this axis [5,6]. The polarization of the compounds is along the *a*-axis. Therefore, the thin films with *a*-axis orientation are preferred for use in many kinds of devices, such as ferroelectric random access memories, piezoelectric micro-actuators, and resonators. The crystallinity and orientation of the Pt bottom electrodes were found to affect the phase transition of paraelectric to ferroelectric in CBTi144 thin films [7].

Most of the reported data on these materials show attractive ferroelectric properties, and some properties such as fatigue have been well studied [8,9]. Retention as one of the important properties has been attracted much attention, nevertheless, the mechanism of retention for CBTi144 thin films is still not clear [10,11]. In this letter, we have investigated the influence of the annealing atmosphere on the properties of $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ ferroelectric thin films. Also, the role of the applied electric field was investigated. The fatigue and retention mechanisms basing

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on depolarization and weak pinning of domain walls have been suggested.

2. Experimental procedure

The CBTi144 thin films were prepared by the polymeric precursor method, as described elsewhere [12,13]. The CBTi144 thin films were spin coated on (111) Pt/Ti/SiO₂/Si substrates by a commercial spinner operating at 5000 revolutions/min for 30 s (spin coater KW-4B, Chemat 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. The pure phase could not be obtained without additional bismuth as reported in the literature [14]. The thin films were annealed at 700 °C for 2 h in a conventional furnace in static and oxygen atmosphere (flux 100 mL/min). Through this process, we have obtained thickness values of about 310 nm for CBTi144 annealed in static air and 280 nm for the film annealed in oxygen atmosphere. The final film thickness was reached by repeating the spin-coating and heat treatment cycles. Phase analysis of the films was performed at room temperature by X-ray diffraction (XRD) using a Bragg–Brentano diffractometer (Rigaku 2000) and CuK α radiation. The microstructure of the thin films was examined using atomic force microscopy (AFM) (Digital Instruments, Nanoscope IIIa). The thickness of the annealed films was measured using scanning electron microscopy (Topcom SM-300) at the transversal section. In this case back scattering electrons were used. A 0.5 mm diameter top Au electrode for the electrical measurements was prepared by sputtering through a shadow mask at room temperature. The electric properties were measured in the Au/CBTi144/Pt/Ti/SiO₂/Si capacitor configuration. 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 or externally generated 8.6 μ s wide square pulses with maximum amplitudes of ± 9 V were used. The J – V measurements were recorded on the Radiant technology tester in the current–voltage mode, with a voltage changing from 0 to +10 V, from +10 to –10 V and back to 0 V. The retention characteristics of the films were measured by observing the time-dependent changes of P^* (switched polarization) and P^\wedge (nonswitched polarization) 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^\wedge , positive pulses were used for both writing and reading. The pulse width for all triangular pulses was 1.0 ms. Time delay between the write pulse and the first read pulse is called the retention time.

3. Results and discussion

The X-ray diffraction data obtained of CBTi144 thin film deposited on platinum coated silicon (111) substrates

and annealed at 700 °C for 2 h in static air and oxygen atmosphere are shown in Fig. 1. CBTi144 films on the platinum-coated silicon substrates showed a high intensity of the (200)/(020) diffraction line compared to the other lines, although the (200) and (020) diffraction lines could not be distinguished from each other. The characteristic orientation is considered to be due to a good matching of atomic arrangements in CBTi144 (100)/(010) and the underlying Pt planes. The characteristic peak for platinum-coated silicon substrates was observed in the range of $38^\circ < 2\theta < 41^\circ$ and no preferred orientation of CBTi144 films was noticed. Since the lattice constants of a (or b) and c of the CBTi144 film is close to 0.5417 and 4.086 nm, the lattice mismatches between the ferroelectric phase and Pt lattice were given as remarkably small as 1.1% and 4.9%, respectively. The characteristic (100)/(010) orientation of the CBTi144 film is based on the good lattice matching of CBTi144 (00 l) with Pt (100) planes.

Fig. 2 shows a typical surface morphology of films annealed in static air and oxygen atmosphere. It can be noted that the films annealed in static air favor a higher nucleation rate, leading to a higher number of crystallites and smaller grain sizes. On the other hand, the nucleation rate for the films annealed in oxygen atmosphere is lower, promoting a lower number of crystallites and therefore leading to an increase in the grain size. The average surface roughness value for the film annealed in static air is 3.2 nm while the average grain size consisting of isotropic round shape is 46 nm. Meanwhile, in the case of the film annealed in oxygen atmosphere the average grain size is 55 nm and the surface roughness is 3.2 nm.

Fig. 3 shows the hysteresis loops of the CBTi144 thin films annealed in different atmospheres. The hysteresis loop for films annealed in static air points out that the polarization process could be easier accomplished comparing with films annealed in oxygen atmosphere leading to a

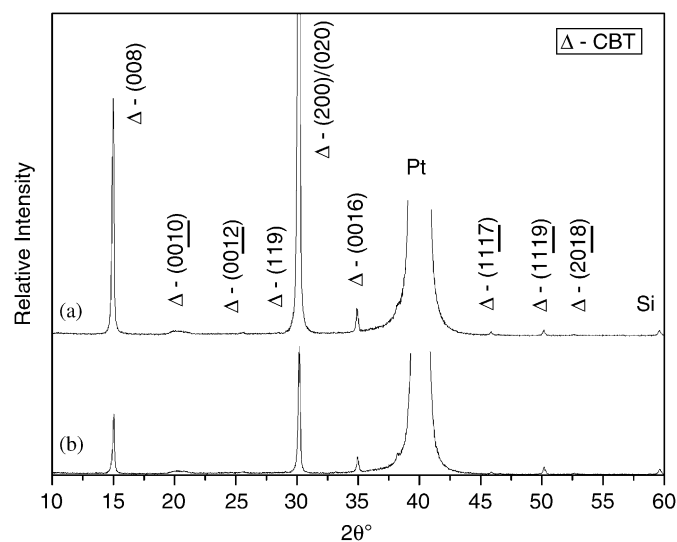


Fig. 1. X-ray diffraction pattern for CBTi144 thin film annealed at 700 °C for 2 h at: (a) static air and (b) oxygen atmosphere.

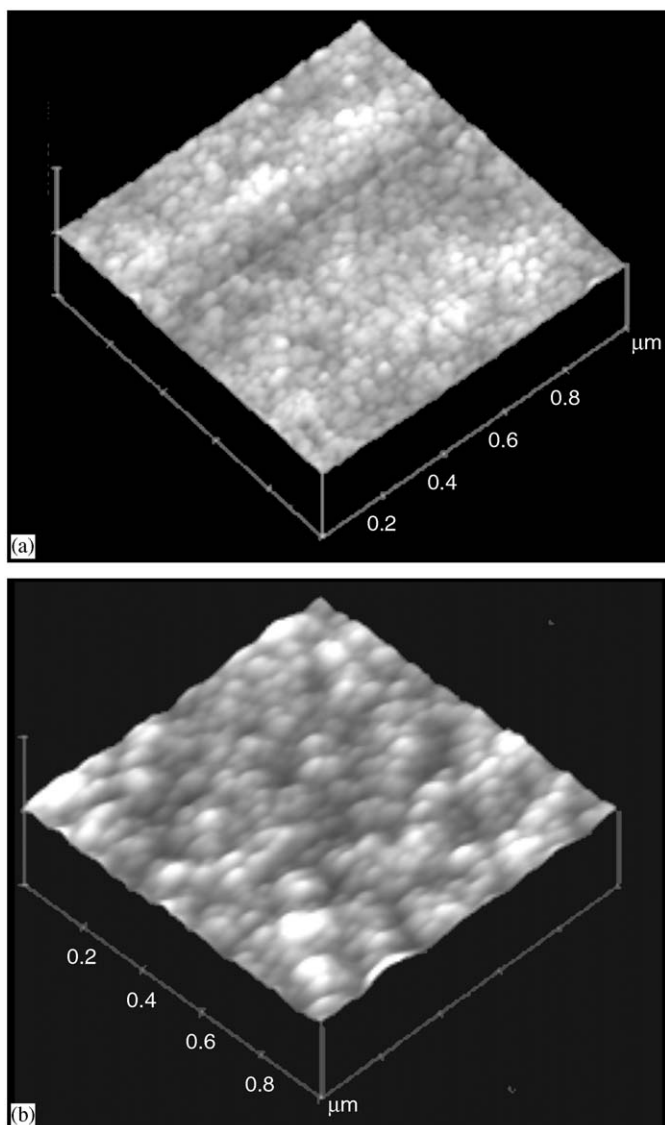
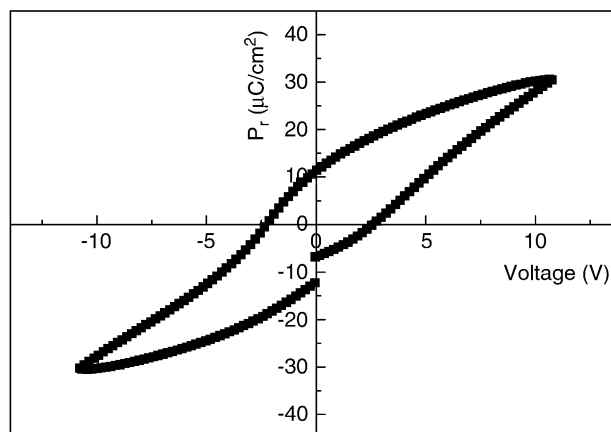
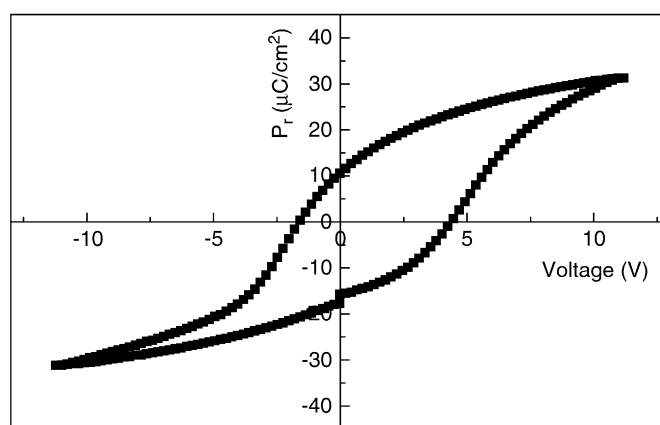


Fig. 2. AFM images for CBTi144 thin films annealed at 700 °C for 2 h at: (a) static air and (b) oxygen atmosphere.

more regularly shaped hysteresis loop. Annealing in oxygen atmosphere should decrease the oxygen vacancy concentration and increase the number of electron holes due to incorporation of oxygen molecules at positively charged oxygen vacancies. However, in materials with p-type conductivity the thermal treatment in oxidant atmosphere increases the defects such as bismuth and titanium vacancies which are located at the grain boundaries and the film–electrode interface and promote a local stoichiometry deviation influencing the shape of the hysteresis loops. Ferroelectricity was observed with remanent polarization of 11.8 $\mu\text{C}/\text{cm}^2$ and drive voltage of 2.4 V for films annealed in static air and 13.1 $\mu\text{C}/\text{cm}^2$ and 3.0 V for films annealed in oxygen atmosphere, respectively. The P_r and E_c values were improved compared with the values obtained for CBTi144 thin films with random orientation [15]. The higher P_r value suggests that the (100) orientation is



(a)



(b)

Fig. 3. P – V hysteresis loop for CBTi144 thin film annealed at 700 °C for 2 h at: (a) static air and (b) oxygen atmosphere.

preferred rather than the (010) orientation with respect to the present CBTi144 film. It should also be noted that the hysteresis loop of the film annealed in oxygen atmosphere shows a significant shift along the electric field axis towards the positive side, which is defined as imprint. The voltage shifts may lead to a failure of the capacitor due to the apparent loss of polarization in one of the remanent states. Consequently, an increase in the coercive voltage in one direction occurs. These two effects may cause a memory failure and can be probably caused by the high concentration of bismuth and titanium vacancies trapped at the film–electrode interface.

The fatigue endurance of CBTi144 thin films was evaluated for films annealed in static air and oxygen atmosphere (Fig. 4). In the figure, P^* is the switched and \hat{P} is the nonswitched polarization between two opposite polarity pulses. The $P^* - \hat{P}$ or $-P^* - (-\hat{P})$ denote the switchable polarization, which is an important variable for nonvolatile memory application. Fatigue resistance was observed up to 10^{10} cycles with an applied pulse voltage of 9 V for the film annealed in static air suggesting that CBTi144 has a good potential for applications in memories. These results are quite different from those obtained

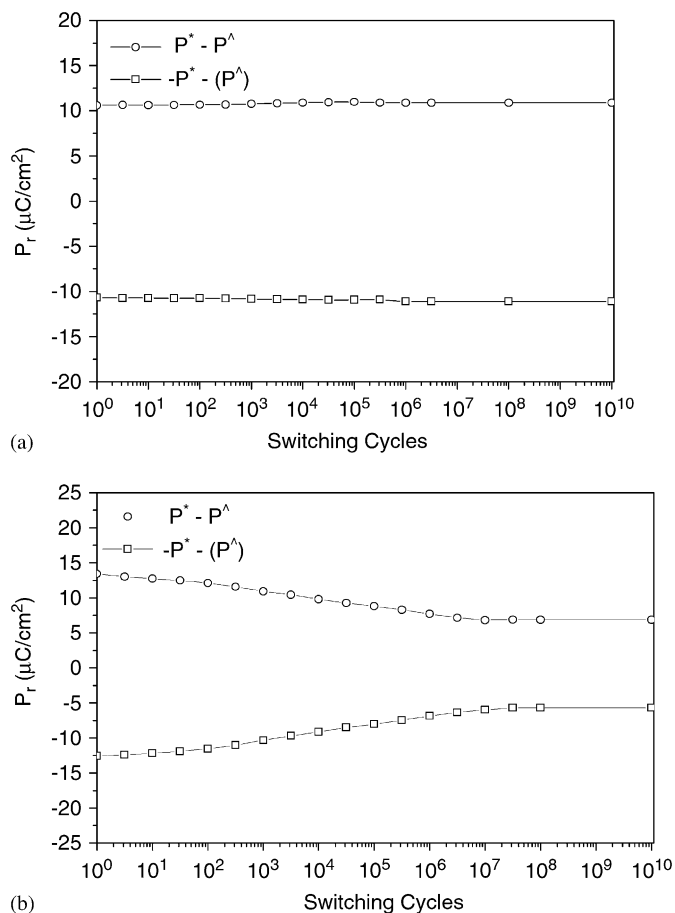


Fig. 4. Fatigue as a function of polarization cycles for CBTi144 thin film annealed at 700 °C for 2 h at: (a) static air and (b) oxygen atmosphere.

for CBTi144 thin films prepared from a precursor solution of metal alkoxides. For such films [7] a strong polarization decay using applied pulse voltages equal to 7 and 9 V was observed. For the films annealed in oxygen atmosphere no fatigue resistance was observed due to the increase in local current around the nucleation sites which can destroy the film–electrode interface and suppress the nucleation of oppositely oriented domains at the surface. In these films an increase in switching polarization leads to a local increase in conductivity in the film–electrode interface region.

Low leakage current density is another important consideration for memory device applications. The insulating properties of the films were found to be dependent on the atmosphere used during thermal treatment. Fig. 5 shows the J – V curves for the CBTi144 films annealed in different atmospheres. As shown, the leakage current density was greatly changed by the atmosphere during thermal treatment. The leakage current density decreased for the films annealed in static air. Such a reduction in leakage current density may be attributed to different defect concentrations at the film–electrode interface.

It can be seen that there are two clearly different regions. The current density increases linearly with the external

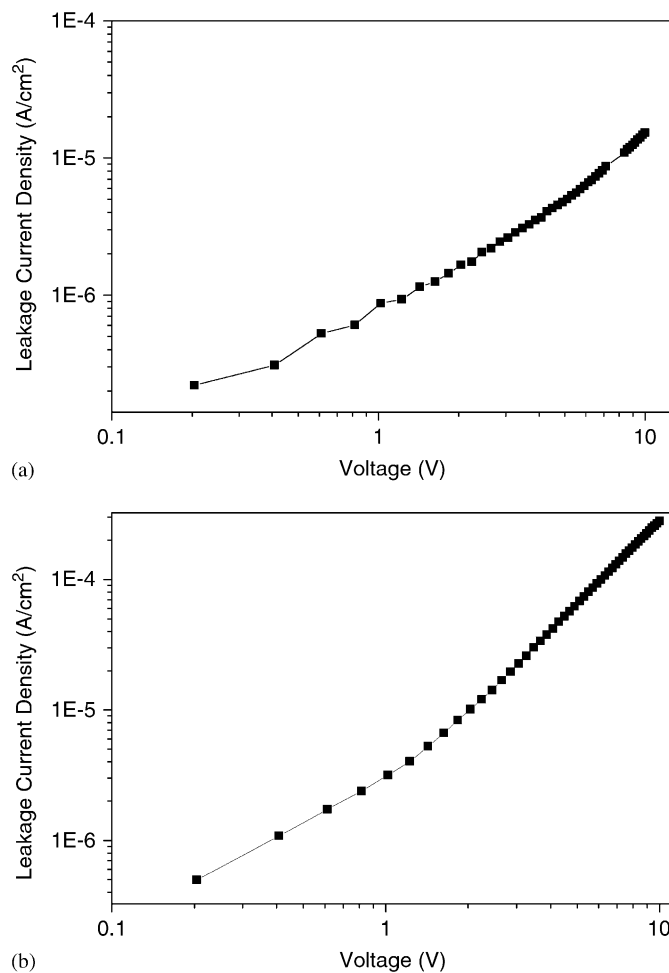


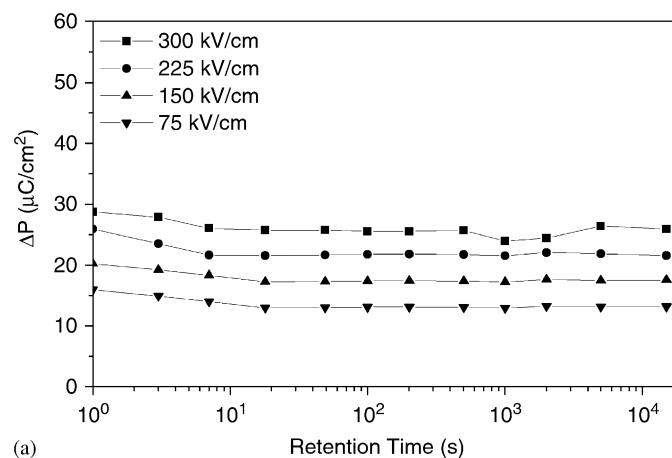
Fig. 5. Leakage current density in dependence of voltage for CBTi144 thin film annealed at 700 °C for 2 h at: (a) static air and (b) oxygen atmosphere.

electric field in the region of low electric field strengths, suggesting an ohmic conduction. At higher field strengths the current density increases exponentially, which implies that at least one part of the conductivity results from Schottky or Poole–Frenkel emission mechanisms. A detailed investigation is in progress to elucidate the predominant conduction mechanism of calcium bismuth titanate films obtained by the polymeric precursor method and will be published in future. The leakage current density at 1.0 V for the film annealed in oxygen atmosphere is 3×10^{-6} and 8×10^{-7} A/cm² for the film annealed in static air. The low current density of the film annealed in static atmosphere is caused by a low defect concentration, particularly by a small deviation from ideal oxygen stoichiometry due to the oriented growth in the a/b -axis direction. A thermal treatment in oxidant atmosphere for materials with p-type conductivity increases the defects such as Bi or Ti vacancies. These results in an increase in conductivity with increasing oxygen content indicating that the mobile carriers are positively charged and that the possibility of hopping of the Bi ion can be considered. As the applied field increases, these defects can strongly

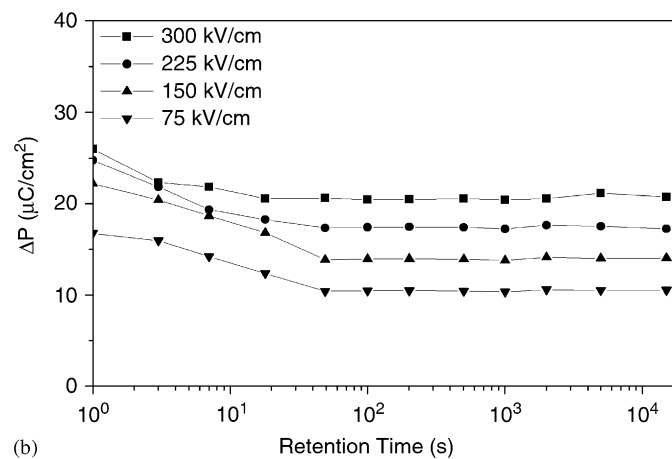
interact with domain boundaries and have significant influence on the conducting process. It seems that mobile vacancies can assemble in polarization extended structures near the domain boundaries and may contribute to an increase in the leakage current.

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. Fig. 6a and b show the long-time retention characteristics of the CBTi144 thin films annealed in static air and oxygen atmosphere, respectively. The retained switchable polarization ($\Delta P = P^* - P^\wedge$) was plotted as a function of retention time from 1 s to 10^4 s at various electric fields from 75 to 300 kV/cm. The high value of initial polarization decayed about 10% and approached a nearly steady-state value after a retention time of 1 s for the films annealed in static air. On the other hand, for the films annealed in oxygen atmosphere the values decreased about 20% indicating that the defects involved in polarization compensation probably originate the strong decay.

The long-time retention characteristics (P^* and P^\wedge) of the CBTi144 films are shown in Fig. 7a and b for the films



(a)



(b)

Fig. 6. Retention time dependence of the retained polarization of the CBTi144 thin film with various applied electric fields (75–300 kV/cm) as a function of different atmospheres: (a) static air and (b) oxygen atmosphere.

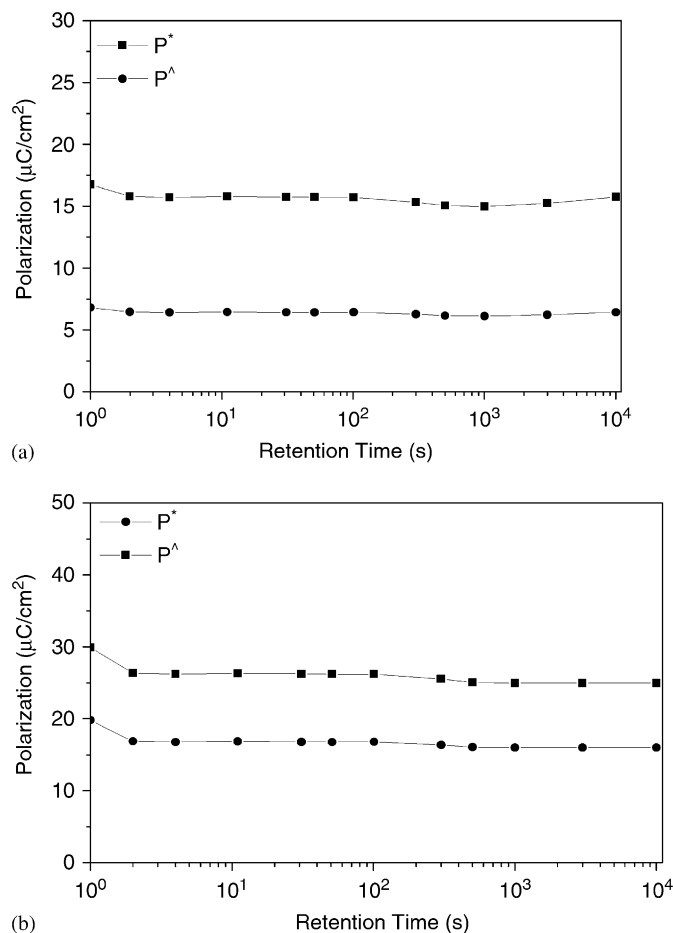


Fig. 7. P^* and P^\wedge of the CBTi144 thin film for retention time up to 10^4 s and applied electric field of 150 kV/cm as a function of different atmospheres: (a) static air and (b) oxygen atmosphere.

annealed in static air and oxygen atmosphere, respectively. The overall time dependence of polarization retention for the CBTi144 film is quite good. After a retention time of 10^4 s, the polarization loss was only about 7% of the value measured at $t = 1.0$ s for a voltage of 9 V in the film annealed in static air. However, this value increased to 16% for the film annealed in oxygen atmosphere. Depolarization fields generated by the redistribution of space charges, defects and dipole charges could be the mechanism for the polarization decay after writing. For the infant period (within 10 s), depolarization fields could be the main contribution to the polarization loss. Similar retention loss behavior has been reported for $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ deposited on Pt/TiO₂/SiO₂/Si [16]. Note that greater than 40% retention loss is often observed for various ferroelectric thin films after 10^4 s even at room temperature [17]. Such behavior has been attributed to a depolarization field which can exist due to the incomplete compensation between the polarization charge and the free charge in the electrodes. 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. Those defects are located in the oxygen sites and compensate the valence deviation introduced by substituting Bi^{3+} by Ca^{2+} . Considering that the CBTi144 thin films show a strong polarization decay in oxygen atmosphere it can be assumed that the bismuth and titanium vacancies can be redistributed and driven by polarization causing a pinning of domain walls. Also, the redistribution of defect charges driven by polarization may cause imprint failure and a decrease in the polarization by compensating the polarization charges. A detailed analysis of these defects should be conducted in order to understand the involved phenomena. Due to the dielectric relaxation, the retained charge is generally less than the switched charge measured from the P - V 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 electrodes, microstructure of the film, temperature, and the details of the test conditions. The understanding and improving 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 will be done to evaluate the merits of calcium bismuth titanate thin films for memory applications.

4. Conclusions

The polarization fatigue and retention characteristics of polar-axis-oriented CBTi144 films deposited on Pt/TiO₂/SiO₂/Si substrates by the polymeric precursor method have been investigated. Excellent fatigue resistance was observed for the films annealed in static air, whereas in the films annealed in oxygen atmosphere, a low fatigue resistance due the pinning of domain walls caused by defects such as bismuth and titanium vacancies was noted. Retention failure tests pointed out that the CBTi144 films have quite good long-time retention characteristics, retaining 90% of the values measured at $t = 1$ s in the films annealed in static air and 80% in the films annealed in oxygen atmosphere.

Polarization charge compensation by the redistribution of defect charges should be considered to better explaining the retention loss, especially in films annealed in oxygen atmosphere. The polar-axis-oriented CBTi144 films annealed in static atmosphere might find future applications as lead-free piezoelectric material in electronic devices.

Acknowledgments

The authors gratefully acknowledge the financial support of the Brazilian financing agencies FAPESP, CNPq and CAPES.

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