Piezoelectric properties of Bi$_4$Ti$_3$O$_{12}$ thin films annealed in different atmospheres


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Received 24 May 2006; accepted 9 August 2006
Available online 25 September 2006

Abstract

Bismuth titanate (Bi$_4$Ti$_3$O$_{12}$—BIT) films were evaluated for use as lead-free piezoelectric thin-films in micro-electromechanical systems. The films were grown by the polymeric precursor method on Pt/Ti/SiO$_2$/Si (1 0 0) (Pt) bottom electrodes at 700 °C for 2 h in static air and oxygen atmospheres. The domain structure was investigated by piezoresponse force microscopy (PFM). Annealing in static air leads to better ferroelectric properties, higher remanent polarization, lower drive voltages and higher piezoelectric coefficient. On the other hand, oxygen atmosphere favors the imprint phenomenon and reduces the piezoelectric coefficient dramatically. Impedance data, represented by means of Nyquist diagrams, show a dramatic increase in the resistivity for the films annealed in static air atmosphere.

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Keywords: A. Ceramics; B. Chemical synthesis; D. Piezoelectricity

1. Introduction

Recently, more and more efforts are being made to develop the nontoxic lead-free piezoelectric materials. Bismuth-layered ferroelectrics are considered to be candidate materials for nonvolatile random access memory (NVFRAM) applications due to their low coercive field and leakage current, long retention, minimal tendency to imprint and little fatigue with usual platinum electrode [1,2]. Bismuth titanate is composed of a triple perovskite unit sandwiched between (Bi$_2$O$_2$)$_2^+$ layers. The monoclinic BIT unit possesses the lattice parameters of $a = 0.5450$, $b = 0.54059$, and $c = 3.2832$ nm, and exhibits the spontaneous polarizations $P_s = 50$ and $4 \, \mu$C/cm$^2$ along $a$- and $c$-axes, respectively [3]. Therefore, films having a larger fraction of $a$-axis-oriented grains should exhibit better ferro- and piezoelectric properties. However, BIT films prefer to grow with $c$-axis perpendicular to the film surface when common Pt (1 1 1) electrodes are used. A suitable electrode with better lattice matching with the long $c$-axis is required in order to fabricate $a$- or $ab$-axis orientation [4]. Because of their complex chemical composition and crystallographical structure, single crystals of these materials are difficult to be grown. Thus, most of the current studies are focused on the applications of thin films [5]. Ferroelectric thin films are constrained by substrates and therefore their properties can be affected by many factors, such as orientation, properties of the substrate (lattice parameters and thermal expansion coefficient) and film thickness. For some applications, as for example in ferroelectric memories and
piezoelectric devices, a large remanent polarization, good fatigue-free characteristics and a high piezoelectric response are required [6].

2. Experimental procedure

BIT thin films were prepared by the polymeric precursor method, as described elsewhere [7]. The films were spin coated on Pt/Ti/SiO₂/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 total Bi content) 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 was reported in literature [8]. The thin films were annealed at 700 °C for 2 h in the conventional furnace in static and oxygen atmosphere (100 mL/min). Through this process, we have obtained thickness values of about 290 nm for BIT annealed in static air and 240 nm for the film annealed in oxygen atmosphere. The film thickness was reached by repeating 10 times the spin-coating and heating 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 Cu Kα radiation. 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 were prepared by evaporation through a shadow mask at room temperature. The electric properties were measured in an Au/BIT/Pt/Ti/SiO₂/Si (100) capacitor structure. Ferroelectric properties of

![X-ray diffraction for BIT thin films annealed at 700 °C for 2 h in: (a) static air and (b) oxygen atmosphere.](image_url)
the capacitor were measured on a Radiant Technology RT6000 A tester equipped with a micrometer probe station in a virtual ground mode. The $J\text{--}V$ 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 piezoelectric measurements were done using a setup based on an atomic force microscope [9] in a Multimode Scanning Probe Microscope with Nanoscope IV controller.

3. Results and discussion

X-ray diffraction data obtained for Bi$_4$Ti$_3$O$_{12}$ thin films deposited with 10 layers on platinum coated silicon (1 1 1) substrates and annealed at 700 °C for 2 h in static air and oxygen atmosphere are shown in Fig. 1a and b, respectively. Polycrystalline Bi$_4$Ti$_3$O$_{12}$ phase is evident for films annealed in static air and oxygen atmosphere. The characteristic peak for platinum coated silicon (1 1 1) substrates was observed in the range of $38^\circ < 2\theta < 41^\circ$. No preferred orientation was observed in the investigated case.

Fig. 2 shows the relationship between the dc bias and capacitance ($C\text{--}V$ curve) for BIT films annealed in static air and oxygen atmosphere at 100 KHz and dc sweep voltage from +10 to $-10$ V. The capacitance dependence on the voltage is strongly nonlinear, confirming the ferroelectric properties of the film resulting from the domain switching. The $C\text{--}V$ curve for the film annealed in static air shows symmetry in the maximum capacitance values that can be observed in the vicinity of the spontaneous polarization switching. This indicates that there is a low concentration of movable ions or charge accumulation at the interface between the dielectric and the electrode. On the other hand, when the capacitor was treated in an oxygen atmosphere, the $V_m$ voltage at which the capacitance is at its maximum

![Capacitance-voltage characteristics for BIT thin films annealed at 700 °C for 2 h in: (a) static air and (b) oxygen atmosphere.](image-url)
The insulating properties of the films were found to be dependent on the atmosphere present during thermal treatment. As shown in Fig. 3, the leakage current density was greatly changed by the atmosphere of 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 improved crystallinity and complete perovskite phase formation. It can be seen that there are two clearly different regions. The current density increases linearly with the external electric field in the region of low electric field strengths, suggesting an ohmic conduction. At higher field the current density increases exponentially, which implies that at least one part of the conductivity results from Schottky or Poole–Frenkel emission mechanisms. The leakage current density at 1.0 V decreases from $3 \times 10^{-6}$ to $5 \times 10^{-7}$ A/cm$^2$ when the films are annealed in static air. The lower leakage current observed for the film annealed in static air may be attributed to probable differences in grain size, density, and surface structure caused by crystallization in two atmospheres. As the applied field increases, defects such as oxygen vacancies interact strongly with domain boundaries and have significant influence on the conducting process. An increase in conductivity with increasing oxygen content indicates that the mobile carriers are positively charged and that the possibility of hopping through the Bi ion can be considered. The oxidation of the BIT surface may be accompanied by the creation of holes captured as follows:

$$\text{(Bi}_2\text{O}_2\text{surface in lattice)} + \frac{3}{4}\text{O}_2 \rightarrow \text{(BiO}''''\text{surface V}''''_{\text{Bi}})\text{complex} + 3\text{h}^* + \frac{1}{2}\text{Bi}_2\text{O}_3$$

Fig. 3. Leakage current density in dependence of voltage for BIT thin films annealed at 700 $^\circ$C for 2 h in: (a) static air and (b) oxygen atmosphere.
In the complex, the \((\text{BiO}_2\text{surface})\) ions act as hole traps, while the \(h^+\) tend to trap electrons. For crystalline BIT, it is known that electrons determine the transport properties, e.g. electrical conductivity, while no such phenomena have been related for holes. This indicates that holes are almost trapped around crystal defects. This means that most of the holes react as follows:

\[
(\text{BiO}_2\text{surface}V_{\text{Bi}}^{\text{V}})_{\text{complex}} + 3h^+ \rightarrow (\text{BiO}_2\text{surface}V_{\text{Bi}}^{\text{X}})
\]

Fig. 4 illustrates the response of impedance spectroscopy at 300 °C for two systems considered in this study. All the semicircular arcs in the complex plane yield to an arc, with the center displaced below the real axis, due to the presence of distributed elements and a relaxation process resulting from the trapped states. Usually, the conductivity of oxide materials is highly dependent upon both the carrier concentration and mobility. The grain boundary resistance is higher for the films annealed in static atmosphere. As the film is annealed in static atmosphere oxygen vacancies become ordered significantly reducing the conductivity. Furthermore, the estimated low conductivity suggests that the film is a very good insulator. A higher oxygen vacancy concentration is observed in films annealed in oxygen atmosphere than in films annealed in static air. The thermal treatment in oxidant atmosphere in materials with p-type conductivity increases the defects as Bi or Ti vacancies. This results in an increase in conductivity with increasing oxygen content indicating that the mobile carriers are positively charged and that the possibility of hopping through the Bi ion can be considered. For the films annealed in oxygen atmosphere the oxygen vacancies are disordered, enabling oxygen ions to migrate and therefore increasing conductivity.

Ferroelectricity of bismuth titanate thin films was performed in a standardized ferroelectric tester and the results are presented in Fig. 5. The hysteresis loop for films annealed in static air pointed that the polarization process could be easier accomplished comparing with films annealed in oxygen atmosphere due to a more regularly shaped hysteresis loop. However, for the film annealed in oxygen atmosphere the trapped charge (\(O_2^\text{O}\)) associated with other defects (\(V_O^{\text{V}}\)) or even defect dipole complexes such as oxygen vacancies associated to bismuth vacancies (\(V_{\text{Bi}}^{\text{V}} - V_O^{\text{V}}\)) located in the grain boundary and in film-electrode interface can promote a local stoichiometry deviation influencing the shape of the hysteresis loops. The remnant polarization was 15 μC/cm² and the coercive field was 60 kV/cm for films annealed in static air and 9 μC/cm² and 40 kV/cm for films annealed in oxygen atmosphere. The spontaneous polarization value in bulk single crystal of bismuth titanate is 50 μC/cm² which is much higher than the corresponding value in our films [11]. This could be due to fact that the loop presented in
Fig. 5 was obtained from the major polarization component vectors lying in the c plane which present low values of remnant polarization. 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 remnant states. Consequently, an increase in the coercive voltage in one direction occurs. These two effects may cause a memory failure. These results are consistent with the C–V measurements and are caused by the high concentration of bismuth and oxygen vacancies trapped in the interface film/electrode.

Fig. 6 shows the piezoelectric hysteresis loop obtained for the films annealed in static and oxygen atmosphere. The hysteresis in the piezoresponse signal is directly associated with the polarization switching and ferroelectric properties of the sample. Although the piezoresponse image shows no activity for the film annealed in oxygen atmosphere a narrow loop is evident. For the film annealed in static air the shape of the loop is similar to a dielectric material indicating that is easier to switch the domains. Here, we point out that it is difficult to compare these values to the piezoelectric coefficients of bulk material since the measurement was performed on a local area that has a relatively intricate field distribution and vibrational modes. Our piezoelectric loop is not similar with the hystereses data once in this case only the contribution of the piezoelectric domains are taken into account. Considering the polycrystalline nature of our films the effective piezoelectric coefficient depends on grain orientation and surface characteristics. Therefore, as expected the piezoelectric response is affected by the annealing in oxygen atmosphere as a consequence of strain energy and pinning effect of charged defects due to the charge transfer to the oxygen. The presence of the white rounded regions on the surface of the films annealed in oxygen atmosphere implies that the surface is very conductive and a switching of the piezoelectric domains is rather difficult to perform.
4. Conclusions

Polycrystalline, homogenous, crack-free BIT thin films were successfully prepared by the polymeric precursor method. The C–V characteristics of the metal-ferroelectric-metal configured capacitors showed a typical butterfly loop.
that confirms the ferroelectric properties of the films related to ferroelectric domain switching. A regularly shaped hysteresis loop is observed after annealing in static air. Annealing in oxygen atmosphere can pin the domain walls caused by defects such as bismuth and titanium vacancies. A higher oxygen vacancy concentration is observed in films annealed in oxygen atmosphere, leading to a more conductive film. Piezoresponse images are strongly affected by the annealing atmosphere.

Acknowledgments

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

References