Review

Ferroelectric and piezoelectric properties of bismuth layered thin films grown on (1 0 0) Pt electrodes


Chemistry Institute, UNESP, Paulista State University, Rua Prof. Francisco Degni s/n, 14801-970 Araraquara, SP, Brazil

ABSTRACT

The effect of film orientation on piezoelectric and ferroelectric properties of bismuth layered compounds deposited on platinum coated silicon substrates was investigated. Piezo-force microscopy was used to probe the local piezoelectric properties of Bi4Ti3O12, CaBi4Ti4O15 and SrBi4Ti4O15 films. Our measurements on individual grains clearly reveal that the local piezoelectric properties are determined by the polarization state of the grain. A piezoelectric coefficient of 65 pm/V was attained after poling in a grain with a polar axis very close to the normal direction. The piezoelectric coefficient and the remanent polarization were larger for a-b axes oriented than for c-axis-oriented films.

© 2007 Elsevier B.V. All rights reserved.

Contents

1. Introduction ................................................................. 10
2. Experimental ............................................................. 11
3. Results and discussion .................................................. 11
4. Conclusions ............................................................... 13
Acknowledgments .......................................................... 13
References ..................................................................... 13

1. Introduction

Piezoelectric materials have been increasingly used to produce microelectromechanical systems (MEMS) due to their excellent electromechanical properties (Bellaiche et al., 2000). Among various piezoelectric materials, lead-based ferroelectric thin films with high piezoelectric coefficient have been extensively studied (Takeguchi et al., 2000). However, with the increasing limitations of lead-based products due to environmental problems, much attention has been paid to investigate lead-free materials. Bismuth-layer-structured ferroelectrics are considered to be candidate materials for lead-free piezoelectrics (Adachi et al., 2005). Bi4Ti3O12 (BIT) is a promising candidate as an alternative material because of its large spontaneous polarization. Also, higher order structures such as SrBi4Ti4O15 (SBTi) and CaBi4Ti4O15 (CBTi144) may have larger...
remanent polarization, due to the increased number of perovskite units generating ferroelectric properties (Simões et al., 2006a; Simões et al., 2006b). SBTi is a member of Aurivillius family with a relatively higher Curie temperature (530 °C). CBTi144 is also a member of this family and its characterized by a high Curie point of about 790 °C and therefore is expected to be useful for special applications at relatively high temperature (Garg et al., 2003). While the effect of film orientation on the ferroelectric properties of epitaxial bismuth layered compounds has been reported in the recent literature (Lee et al., 2002) few works have mentioned the electromechanical properties of these films (Lebihan, 1989). Electromechanical properties of these films are also influenced by the composition and orientation of the grains. Various techniques have been used to estimate the piezoelectric properties of the ferroelectric thin films, such as atomic force microscopy (AFM), laser interferometry and continuous charge integration. In comparison with other techniques, the advantages of AFM are: (a) it can probe the properties of individual grains on the nanoscale, and (b) it can visualize and control the ferroelectric domain during measurement. In this paper, we further report the poling effects on the local piezoelectric coefficients. We also clearly show that the local piezoelectric properties are determined by the polarization state in the grain.

2. Experimental

Calcium citrate (Synth), titanium isopropanoxide (Hulls AG), bismuth oxide (Aldrich) and strontium carbonate (Aldrich), were used as raw materials. The precursor solutions of calcium, bismuth, strontium and titanium were prepared by adding the raw materials to ethylene glycol and concentrate aqueous citric acid under heating and stirring. Appropriate quantities of Ca, Ti, Sr, and Bi solutions were mixed and homogenized by stirring at 90 °C. The molar ratio of metal: citric acid: ethylene glycol was 1:4:16. The viscosity of the resulting solution was adjusted to 20 cP by controlling the water content using a Brookfield viscosimeter. The BIT, SBTi and CBTi144 thin films were spin coated on (1 0 0)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 mass in the solution) 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 the literature. The thin films were annealed at 700 °C for 2 h in a conventional furnace. Through this process, we have obtained thickness values of about 300 nm for all systems, reached by repeating the spin-coating and heat treatment cycles. Phase analysis was performed at room temperature by X-ray diffraction (XRD) in Bragg-Brentano geometry (Rigaku 2000) at Cu Kα radiation. Furthermore, topography and thickness were examined using atomic force microscopy (AFM) (Digital Instruments, Nanoscope IV) and scanning electron microscopy (Topcom SM-300), respectively. The top Pt-electrodes were prepared by photolithography with 8 × 10⁻⁴ mm² dot area. The ferroelectric properties of the capacitors were measured with a Radiant Technology Tester RT6000 A in a virtual ground mode. The piezoelectric measurements were done using a setup based on an atomic force microscope in a multimode scanning probe microscope with Nanoscope IV controller.

3. Results and discussion

Fig. 1 shows the XRD results of all investigated systems. The SBTi and BIT films present a polycrystalline nature with c axis orientation. Meanwhile, CBTi144 films showed a high intensity of the (2 0 0)/(0 2 0) diffraction line compared to the other lines, although the (2 0 0) and (0 2 0) diffraction lines could not be distinguished from each other. The characteristic orientation is considered to be due to good matching of atomic arrangements in CBTi144 (1 0 0)/(0 1 0) and underlying Pt planes. Since the lattice constants a (or b) and c of the CBTi144 film are close to 0.5417 and 4.086 nm, the lattice mismatches between the ferroelectric phase and Pt were given remarkably small as 1.1% and 4.9%, respectively. The characteristic (1 0 0)/(0 1 0) orientation of the CBTi144 film is based on the good lattice matching of CBTi144 (0 0 1) with Pt (1 0 0) planes. From the technical point of view, random-oriented films are more favorable than (0 0 1) oriented films. Therefore, this suggests that CBTi144 films deposited on Pt electrodes have a suitable orientation to reach excellent ferroelectric and piezoelectric properties.

Three-dimensional images of BIT, SBTi and CBTi144 thin films annealed at 700 °C for 2 h in static atmosphere can be seen in Fig. 2a–c. The films were characterized by a smooth surface with a homogeneous and crack-free microstructure devoid of pores. An important aspect is the morphology difference between those films. BIT film contains a plate-like morphology while CBTi144 and SBTi a granular structure. The surface roughness of BIT film is around 17.0 nm (grain size of 130 nm) while for CBTi144 and SBTi films are around 6 nm (46 and 89 nm, respectively). Although the electrical properties is affected by composition and film orientation, in our case it seems that the preferred growth of the main phase is being crucial in the improvement of the ferroelectrical and piezoelectrical properties.
Fig. 3 shows polarization hysteresis loops of the bismuth layered compounds. Remanent polarizations of $13 \mu C/cm^2$ with coercive field of 76 kV/cm were observed for the BIT films. The small $P_r$ of the BIT films originates from the stronger contribution of the crystallites grown in the $c$-axis direction. The SrBi$_4$Ti$_4$O$_{15}$ films showed poor ferroelectric properties. The hysteresis loop was not saturated even at 350 kV/cm, $P_r$ was only $5.4 \mu C/cm^2$ and the coercive field ($E_c$) was as high as 80 kV/cm. These results were similar to those reported by Irie and Miyayama (Irie and Miyayama, 2001). They found that SrBi$_4$Ti$_4$O$_{15}$ single crystals in $a$ and $b$ axes orientations showed typical ferroelectric behavior with $P_r = 29 \mu C/cm^2$, whereas dielectric behavior was observed for $c$-axis orientation. Meanwhile, in the case of CBTi$_{144}$ films, $P_r$ and $E_c$ values were improved compared with the values obtained for CBTi$_{144}$ thin films with random orientation (Gruverman et al., 1997). The higher $P_r$ value suggests that the $(100)$ orientation is preferred rather than the $(010)$ orientation with respect to the present CBTi$_{144}$ film. In this film, the remanent polarization was equal to $14 \mu C/cm^2$ and coercive field equal to 64 kV/cm (Fig. 2). No imprint phenomenon which causes a significant shift along the electric field axis towards the positive side was observed. These results clearly demonstrate that controlling the orientation of grains in a film is a key point to improve the ferroelectric properties.

Due to the anisotropic characteristics, the dielectric properties of bismuth layered thin films are always determined by the crystal structure and orientation, which defines the magnitude of switchable domains that contribute to the dielectric displacement. The $C-V$ results are shown in Fig. 4. The butterfly-shape curves that characterize every ferroelectric material are consistent with the other electrical measurements and the microstructural data. The two peaks, which characterize spontaneous polarization switching, are clearly shown in Fig. 3. Also, the curve displays symmetry in the maximum capacitance values that can be observed in the vicinity of the spontaneous polarization switching. All curves are symmetric around the zero bias axes, indicating that the films
contain few movable ions or charge accumulation at the film-electrode interface. From C–V the measured value of relative dielectric constant at a frequency of 1 MHz is 265 for BIT, 35 for SBTi and 1535 for CBTi144 films. As we expected, the lower value of dielectric constant is related to the contribution of c-axis orientation, which also translates to low piezoelectric response.

The \( d_{33} \) (V) hysteresis loops are shown in Fig. 5. The \( d_{33} \) value of BIT is close to 40 pm/V, and approaches the reported value for a BIT single crystal (Saneto and Cross, 1982). An enhancement of piezoelectric coefficient was observed for the CBTi144 film. The maximum \( d_{33} \) value, 65 pm/V approaches the reported value for a CBTi144 single crystal (Kang et al., 1999). The enhancement of polarization could be caused by the \( a/b \) axis orientation of the ferroelectric films due to the preferred orientation of the Pt substrate. As can be seen, the hysteresis loop shows an offset in the vertical direction which is probably caused by the clamping effect and the existence of an ultra-thin air gap between the tip and the sample which might lower the actual voltage drop across the film (Gruverman et al., 1998; Kato et al., 2001). The presented values reported for our CBTi144 films suggest that this material can be considered as a viable alternative for lead-free piezo-ferroelectric devices. In comparison with other lead-free ferroelectrics, 65 pm/V is much higher than the \( d_{33} \) value of \( \text{SrBi}_2\text{Ta}_2\text{O}_9 \) films (17 pm/V) (Kholkine et al., 1996) and Nd-doped \( \text{Bi}_4\text{Ti}_3\text{O}_{12} \) (38 pm/V) (Fu et al., 2003). The coercive voltage obtained in this manner is about 5 V. This value is comparable to that derived from the polarization measurements and is lower than that for sol–gel derived films deposited onto Pt foil which present an extremely high piezoelectric coefficient of 180 pm/V and a coercive voltage equal to 30 V (Kalinin and Bonnell, 2001).

4. Conclusions

In summary, we investigated the dependence of piezoelectric and ferroelectric properties of several bismuth layered compounds grown by the polymeric precursor method upon film orientation. The films were characterized by a smooth surface with a homogeneous and crack-free microstructure devoid of pores. Highly SBTi c-axis-oriented films grown on (1 0 0) Pt electrodes show weak piezoelectric properties. Meanwhile, polar-axis-oriented CBTi144 films exhibited excellent and improved ferro- and piezoelectric properties. The polar-axis-oriented CBTi144 films would open up possibilities for devices with Pb-free piezoelectric materials.

Acknowledgments

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

References

Adachi, Y., Su, D., Murali, P., Setter, N., 2005. Ferroelectric and piezoelectric properties of lanthanoid-substituted \( \text{Bi}_4\text{Ti}_3\text{O}_{12} \) thin films grown on (1 1 1)Pt and (1 0 0)IrO2 electrodes. Appl. Phys. Lett. 86, 172904.


