Microstructure and electric properties of (104)/(014)-oriented Bi$_{3.15}$Nd$_{0.85}$Ti$_3$O$_{12}$ films on Pt (111)/Ti/SiO$_2$/Si by sol–gel method

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Received 19 January 2007; accepted 20 March 2007
Available online 19 April 2007

Abstract

Bi$_{3.15}$Nd$_{0.85}$Ti$_3$O$_{12}$ (BNdT) thin films with predominant (104)/(014) orientation were fabricated directly on (111)Pt/Ti/SiO$_2$/Si substrates through a sol–gel process. The volume fraction of (104)/(014)-oriented grains in the film was estimated to be about 65% according to X-ray pole figure. The BNdT film is dense and uniform and consists of columnar grains penetrating the whole film thickness. The (104)/(014)-oriented BNdT film capacitors showed excellent ferroelectric properties with $2P_r = 46.4$ μC/cm$^2$ and $E_c \approx 140$ kV/cm. The films also exhibit excellent piezoelectric property, with high piezoelectric coefficient $d_{33} \approx 17$ pm/V.

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Keywords: Ferroelectrics; Thin film; Orientation; Piezoelectricity

1. Introduction

Ferroelectric lanthanide-substituted Bi$_4$Ti$_3$O$_{12}$, such as Bi$_{3.15}$Nd$_{0.85}$Ti$_3$O$_{12}$ (BNdT) films, are being studied for use as nonvolatile digital memories due to their excellent fatigue endurance on Pt electrodes [1–4]. In high-density memories of Gbit memory density, the individual cells will have a lateral size below 100 nm. This size corresponds to the order of magnitude of the grain diameter in polycrystalline films. Therefore, the random grain orientation of the films should result in a nonacceptable cell-to-cell nonuniformity of the ferroelectric properties within the memory array [5]. The use of uniformly oriented ferroelectric films is most probably the only way to avoid such nonuniformity problems in high-density ferroelectric memories.

Bi$_4$Ti$_3$O$_{12}$ (BTO) is monoclinic with the space group B1$a_1$ but can be considered pseudo-orthorhombic with $a=0.545$ nm, $b=0.541$ nm and $c=3.283$ nm. The anisotropy of crystal structure leads to the anisotropic ferroelectric properties of BTO. It is observed that for nonsubstituted BTO single crystals, the major component of spontaneous polarization ($P_s$) is directed along the $a$ axis ($\approx 50$ μC/cm$^2$) and the component along the $c$ axis is very small ($\approx 4$ μC/cm$^2$) [6]. For BNdT, a similar ferroelectric anisotropy was confirmed [1,2,4,7]. It is therefore desirable to grow non-$c$-axis-oriented BNdT thin films in order to achieve a higher polarization component along the film normal. Unfortunately, BNdT films are easily grown with the $c$-axis perpendicular to the film plane (i.e. $c$-axis orientation) on Pt-coated Si substrates [8]. Recently, Lee et al. [9] fabricated (104)-oriented Bi$_{3.54}$Nd$_{0.46}$Ti$_3$O$_{12}$ films on buffered Si(100) substrates using an intermediate SrRuO$_3$ epitaxial layer, and a (111)-oriented Pt conducting layer grown on the YSZ(100)/Si(100) substrate served as template for the subsequent growth of (111)-oriented SrRuO$_3$ layers and (104) oriented Bi$_{3.54}$Nd$_{0.46}$Ti$_3$O$_{12}$ films. Here, we report predominant (104)/(014)-oriented BNdT films directly grown on (111)Pt/Ti/SiO$_2$/Si substrates without any buffer layer and study the microstructure, dielectric, ferroelectric and piezoelectric properties.

2. Experimental

The BNdT films were deposited on (111)Pt/Ti/SiO$_2$/Si(100) substrates using a sol–gel process. The preparation of precursor
solution for the coating was reported previously [3]. The as-deposited films were pyrolyzed at 450 °C for 30 min in air, followed by annealing at 750 °C for 1 h in flowing O2 to produce the layered-perovskite phase. The deposition–crystallization cycles were repeated 12 times to obtain the desired thickness. A heating rate of 40 °C/min was used during crystallization. For the fabrication of BNdT capacitors, Pt top electrodes of typically 0.24 mm² in size were deposited by sputtering using a shadow mask. Ferroelectric measurements were performed using a TF Analyzer 2000 ferroelectric tester (Aix-ACCT). Low-frequency impedance analyzer (HP-4192A) was used to determine the dielectric properties of the films.

3. Results and discussion

The crystallographic orientation of the BNdT films was examined using X-ray diffraction (XRD) performed on a Philips X’Pert MRD four-circle diffractometer (Cu Kα radiation). Fig. 1(a) and (b) shows the XRD θ–2θ scan and pole figure of BNdT film and the fixed 2θ angle used to record the pole figure was 30.26° corresponding to the BNdT (117) planes. XRD pattern is indexed according to the standard powder diffraction data of Bi₃.6Nd0.4Ti₃O₁₂ [10]. In the standard data, the (117) reflection is the strongest peak and its intensity is about 100 times that of (014). As shown in Fig. 1(a), the (014) peak is a little bit stronger than the (117) peak, suggesting that the film is pre-dominantly (104)/(014)-oriented. It should be noted that only the (014) reflection is present because (104) is prohibited due to systematic absences [2]. There are two rings at ψ ≈ 36° and 84° in Fig. 1(b) and they correspond to the (117)/(117) and (117)/(117) reflections, respectively. The pole figure confirms the predominant (104)/(014) orientation of the film, because the angle between the (104) plane and the diffracting (117) plane is 36.4° and the angle between (104) and (117) is 84.1°. The pole figure exhibits background intensities in the range of 20–80 counts, while the maximum intensity at the ring ψ ≈ 36° is about 790 counts. This indicates that the BNdT film is a mixture of the (104)/(014) orientation and random orientation. According to the X-ray pole figure, the volume fraction of the (104)/(014)-oriented grains in the film can be estimated to be around 65%, which is calculated by a comparison of the integrated intensities of the two rings to the total integrated intensities in Fig. 1(b).

The microstructure of the BNdT films was investigated by transmission electron microscopy (TEM) (Tecnai G20) and atomic force microscopy (AFM) (Dimension TM 5000). Fig. 2(a) and (b) shows cross-sectional TEM images of the BNdT film taken at different magnifications. It can be seen from Fig. 2(a) that the ~400 nm thick film consists of large columnar grains of about 200 nm in lateral size. Almost all columnar grains penetrate the whole film thickness. The surface morphology is determined by the shapes of the grains, resulting in a rather rough surface. Fig. 2(b) taken at a higher magnification presents the Bi₂O₂ layers or (002) planes within a (104)-oriented grain and the selected-area electron diffraction pattern of the grain is shown.
These planes make an angle of 56° with the (104) plane, i.e., with the substrate plane. The well-pronounced parallel structure of the (002) planes confirms the good crystallinity of the film. The AFM image in Fig. 3 shows the surface morphology of the film. The film was dense and uniform with grain size of about 50–150 nm in diameter. The rms roughness was about 12.5 nm, which is in agreement with 10–15 nm of (104)-oriented BNdT epitaxial film reported by Garg et al. [11].

The butterfly shape of the dielectric constant ($\varepsilon_r$)—and loss tangent ($\tan\delta$)—electric field curves (not shown here) confirmed the excellent ferroelectric characteristic of the BNdT film. Both the $2P_r$ and $2E_c$ values increase with increasing the applied field and $2P_r$ values increase rather steeply at lower applied electric field but do not change much beyond 450 kV/cm. The measured $2P_r$ and $E_c$ values of the capacitor are about 46.4 μC/cm² and 140 kV/cm, respectively, for a maximum applied electric field of 630 kV/cm. Interestingly, the $2P_r$ of 46.4 μC/cm² of our film is a little larger than the value reported for (104)/(014)-oriented BNdT epitaxial films ($2P_r=40$ μC/cm²) [2]. This difference is likely due to the different orientation degree and the residual stress arising from completely different processing methods adopted in the two cases. Another interesting observation is that the $E_c$ value of our film is larger than Garg et al. [2] and Li et al. [3] reported. Reasons for this are not clear at the moment, but the following factors might attribute to the difference. Firstly, it is reported the polarization switching in films with finer grains is usually more difficult. The domain walls in larger and platelet grains are easier to be switched under external field, while smaller domains in peg-like shape seem more stable [12,13]. Secondly, ferroelectric property has a strong dependence on film orientation. Different orientation might contribute to different coercivity.

Piezoresponse investigations of the BNdT films were performed using an Autoprobe CP-Research (Thermomicroscopes) atomic force microscope in contact mode equipped with PtIr-coated tips (Nanosensors, ATEC-EFM) with an elastic constant of about 2.5 N/m. Details on this method are available elsewhere [14]. Fig. 5 shows piezoelectric hysteresis loop of the BNdT film. The effective remanent piezoelectric coefficient $d_{33}$ of the BNdT film is about 17 pm/V, which is higher than 4.3 pm/V of (001)-, (117)-oriented Bi$_{3.25}$Nd$_{0.75}$Ti$_3$O$_{12}$ film and is comparable with 16.9 pm/V of (111)- and (110)-oriented Bi$_{3.25}$Nd$_{0.75}$Ti$_3$O$_{12}$ film [15].

4. Conclusion

In conclusion, Bi$_{3.15}$Nd$_{0.85}$Ti$_3$O$_{12}$ (BNdT) thin films with predominant (104)/(014) orientation were fabricated directly on standard-type (111)Pt/Ti/SiO$_2$/Si substrates through a sol–gel process. The volume fraction of (104)/(014)-oriented grains in the film was estimated to be about 65% according to X-ray pole figure. The BNdT film is dense and uniform and consists of columnar grains penetrating the whole film thickness. The $\varepsilon_r$–$E$ characteristic has typical butterfly pattern which confirmed excellent ferroelectric property ($2P_r=46.4$ μC/cm², $E_c=140$ kV/cm) of (104)/(014)-oriented BNdT film. The film also exhibits excellent piezoelectric property, with high piezoelectric coefficient $d_{33} \approx 17$ pm/V.

Acknowledgements

The authors are grateful for the financial support from the National Science Foundation of China (Grant No.10474019),...
the Excellent Young Teachers Program of MOE, P. R. C. (EYTP), and the Natural Science Foundation of Hubei Province, China.

References