Oriented growth and ferroelectric anisotropy of sol–gel derived Bi$_{3.15}$Nd$_{0.85}$Ti$_3$O$_{12}$ thin films on Nb-doped SrTiO$_3$

Chaojing Lu$^{1,2,3}$, Wanneng Ye$^{1,2}$, Yajun Qi$^2$, Xiaolin Liu$^2$, Stephan Senz$^4$, and Dietrich Hesse$^4$

1 Laboratory of Fiber Materials and Modern Textile, the Growing Base for State Key Laboratory, Qingdao University, Qingdao 266071, P.R. China
2 Department of Materials Science and Engineering, Hubei University, Wuhan 430062, P.R. China
3 Key Laboratory of Education Ministry on Low Dimensional Materials and Application Technology, Xiangtan University, Xiangtan, Hunan 411105, P.R. China
4 Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany

Received 5 February 2008, accepted 10 June 2008
Published online 16 July 2008

PACS 61.05.cp, 68.37.Lp, 68.55.Jm, 77.80.Fm, 77.84.Dy, 81.20.Fw

Ferroelectric Bi$_{3.15}$Nd$_{0.85}$Ti$_3$O$_{12}$ (BNdT) thin films were grown through a cheap and simple sol–gel process on Nb-doped SrTiO$_3$ single crystal substrates of (001) and (011) orientations. The films containing 30% (100)/(010)-oriented plus 18% (119)-oriented columnar grains were obtained on Nb: SrTiO$_3$(001) using a rapid heating during crystallization, while the films containing 19% c-axis-oriented prolate grains on Nb: SrTiO$_3$(001) using a low heating rate. Anisotropic ferroelectric properties were determined, with a remanent polarization $2P_r = 28.4$ μC/cm$^2$ in the film with predominant 100/010/119 orientations, but only $2P_r = 5.7$ μC/cm$^2$ in the predominantly c-axis-oriented film. The ferroelectric anisotropy confirms that the polarization vector of BNdT is close to the c-axis.
Oriented growth and ferroelectric anisotropy of sol–gel derived Bi$_{3.15}$Nd$_{0.85}$Ti$_3$O$_{12}$ thin films on Nb-doped SrTiO$_3$

Chaojing Lu$^{1,2,3}$, Wanneng Ye$^{1,2}$, Yajun Qi$^2$, Xiaolin Liu$^2$, Stephan Senz$^4$, and Dietrich Hesse$^*$

1 Laboratory of Fiber Materials and Modern Textile, the Growing Base for State Key Laboratory, Qingdao University, Qingdao 266071, P.R. China
2 Department of Materials Science and Engineering, Hubei University, Wuhan 430062, P.R. China
3 Key Laboratory of Education Ministry on Low Dimensional Materials and Application Technology, Xiangtan University, Xiangtan, Hunan 411105, P.R. China
4 Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany

Received 5 February 2008, accepted 10 June 2008
Published online 16 July 2008

PACS 61.05.cp, 68.37.Lp, 68.55.Jm, 77.80.Fm, 77.84.Dy, 81.20.Fw

*Corresponding author: e-mail cjlu@qdu.edu.cn, Phone: +86-532-85950217

Ferroelectric Bi$_{3.15}$Nd$_{0.85}$Ti$_3$O$_{12}$ (BNdT) thin films were grown through a cheap and simple sol–gel process on Nb-doped SrTiO$_3$ single crystal substrates of (001) and (011) orientations. The films containing 30% (100)/(010)-oriented plus 18% (119)-oriented columnar grains were obtained on Nb:SrTiO$_3$(011) using a rapid heating during crystallization, while the films containing 19% c-axis-oriented prolate grains on Nb:SrTiO$_3$(001) using a low heating rate. Anisotropic ferroelectric properties were determined, with a remanent polarization $2P_r = 28.4$ $\mu$C/cm$^2$ in the film with predominant 100/010/119 orientations, but only $2P_r = 5.7$ $\mu$C/cm$^2$ in the predominantly c-axis-oriented film. The ferroelectric anisotropy confirms that the polarization vector of BNdT is close to the $a$-axis.

1 Introduction Ferroelectric thin films have been widely investigated in view of their applications in non-volatile memories, piezoelectric microactuators and resonators. Rare-earth element-substituted Bi$_x$Ti$_3$O$_{12}$ films are promising due to their fatigue endurance on Pt electrodes [1, 2]. Bi$_{12.5}$La$_{0.5}$Ti$_3$O$_{12}$ and Bi$_{12.5}$Nd$_{0.5}$Ti$_3$O$_{12}$ (BNdT) films have received attention for their large remanent polarization $P_r$ [3–11]. Bi$_3$Ti$_3$O$_{12}$ is monoclinic with the space group $B1a1$ but can be considered pseudo-orthorhombic with $a = 0.545$ nm, $b = 0.541$ nm and $c = 3.283$ nm. For non-substituted Bi$_3$Ti$_3$O$_{12}$ single crystals, the major component of spontaneous polarization ($P_s$) lies along the $a$-axis ($\approx 50$ $\mu$C/cm$^2$); the component along the $c$-axis is very small ($\approx 4$ $\mu$C/cm$^2$) [12]. This ferroelectric anisotropy requires the growth of non-c-axis-oriented films to achieve large $P_s$ values in planar-type capacitors. While BNdT films having a larger fraction of $a$-axis (or near-$a$-axis) oriented grains should exhibit better ferro- and piezoelectric properties in planar-type capacitors, predominantly $c$-axis oriented BNdT films with interdigitated electrodes on their top surfaces are attractive for microwave device application.

Recently, the growth of rare-earth element-substituted Bi$_3$Ti$_3$O$_{12}$ films with $a/b$-axes orientation [3, 4, 13–16] and with (104)/(014) orientation [5, 8, 10, 11, 15–18] by the elaborative pulsed laser deposition (PLD) or metal-organic chemical vapor deposition (MOCVD) methods were reported and all this work confirmed the crucial role of the crystallographic orientation. Unfortunately, there are only few reports on such oriented films grown by chemical solution deposition [7, 19–22]. We previously reported on a cheap and simple sol–gel route to grow BNdT films with predominant $a/b$-axes orientation or with predominant (104)/(014) orientation on (111)Pt/Ti/SiO$_2$/Si and on the large anisotropy of their ferro-, piezo- and dielectric properties [7, 22]. This article presents the oriented growth of BNdT films on conducting Nb-doped SrTiO$_3$ single crystals with (001)- and (011)-plane surfaces, quantifies the
amount of the predominant orientation, considers their microstructure, and characterizes their ferroelectric properties.

2 Experimental

Electrically conductive (001)- and (011)-oriented SrTiO$_3$ single crystals doped with 0.5% of Nb were used as substrates. All the BNdT thin films were deposited on Nb: SrTiO$_3$ substrates using a sol–gel process. Appropriate amounts of Bi(NO$_3$)$_3$, 5H$_2$O, Nd(CH$_3$COO)$_3$, and Ti(OCH$_3$)$_4$ were dissolved in an acidic solution. 4 mol% excess bismuth nitrate was added to compensate for the Bi loss during annealing. The as-deposited films were pyrolyzed at 450 °C in air, followed by annealing at 750 °C in flowing oxygen. A heating rate of 80 K/s was used in the case of BNdT films deposited on Nb: SrTiO$_3$(011) whereas it was 40 K/min for the films on Nb: SrTiO$_3$(001). The deposition-crystallization cycles were repeated many times to obtain the desired thickness. Each single-annealed layer is ~15 nm thick.

The obtained BNdT thin films were investigated by X-ray diffractometry (XRD) in $\theta$–2$\theta$ scans and $\phi$–$\psi$ pole figures applying a Philips X’Pert MRD four-circle diffractometer using Cu K$_\alpha$ radiation. The fixed 2$\theta$ angle of 30.26° was used to record pole figures, corresponding to BNdT (117) planes. For the fabrication of BNdT capacitors, Pt top electrodes of 0.24 mm$^2$ size were deposited by sputtering using a shadow mask. Ferroelectric measurements were performed on a TF Analyzer 2000 ferroelectric tester (aixAcct) at a frequency of 1 kHz. The microstructures of the BNdT thin films were investigated using transmission electron microscopy (TEM) on a Tecnai G$^2$ microscope operated at 200 kV.

3 Results and discussions

3.1 Preferred orientation of BNdT films on Nb: SrTiO$_3$(001)

Figure 1(a) shows a XRD $\theta$–2$\theta$ scan of the BNdT film deposited on Nb: SrTiO$_3$(001). The peaks of the film are indexed according to the standard powder diffraction data of Bi$_{3.15}$Nd$_{0.85}$Ti$_3$O$_{12}$ [23]. In the standard data, the 117 reflection is the strongest peak. In Fig. 1(a), the 00/10/00/04 peaks are much stronger than the 117 peak, suggesting that the film is predominantly c-axis-oriented. Figure 1(b) displays the X-ray pole figure of the film recorded from the BNdT (117) reflection. The four diffraction peaks at $\psi \approx 51^\circ$ in the pole figure correspond to the (117)/(1 1 7) and (1 1 7)/(1 1 7) reflections. Because of the angles $\angle (001):\{117\} = 50.76^\circ$, the four peaks confirm the predominant c-axis orientation of the film, with good in-plane alignment between the c-axis-oriented BNdT grains and the Nb: SrTiO$_3$(001) substrate. BNdT {117} planes have a tilt angle of 50.7° with respect to the BNdT (001) plane, which is parallel to the substrate surface. The background intensities of the pole figure are in the range of 10−70 cps, while the maximum intensity of the peaks at $\psi \approx 50.76^\circ$ is about 11800 cps, indicating a mixture of c-axis orientation and random orientations. The background ring at $\psi \approx 51^\circ$ stems from a small amount of c-axis-oriented BNdT grains with a random in-plane orientation. According to the pole figure, the volume fraction of the c-axis-oriented grains in the film can be estimated to be around 19% by calculating as follows: The numerator of the fraction is the sum of the integral intensity of the four peaks and that of the background ring at $\psi = 0^\circ$ and 90°, respectively.

Figure 2(a) is a cross-sectional TEM image of the BNdT film grown on Nb: SrTiO$_3$(001) and Figure 2(b) shows an enlarged image displaying the Bi$_2$O$_3$ layers or (002) planes within the BNdT grains 1–5 in Fig. 2(a). It can be seen that the 250 nm thick film consists of prolate grains. The (002) planes of the grains 2–4 are parallel to the substrate surface, indicating the c-axis-orientation of the grains. The grains 1 and 5 are non-c-axis oriented because their c-axes tilt away from the film growth direction. Detailed TEM observations confirm the predominant c-axis orientation of the film, in accordance with the XRD analysis.
It is well known that layered perovskites such as Bi$_4$Ti$_3$O$_{12}$ have much faster growth rate in the $a$–$b$ plane than along the $c$-axis [12, 24]. The microstructure of the BNdT film can be understood in terms of the anisotropic growth of BNdT grains, and considering the $c$-axis oriented grains having a higher nucleation density than the $a/b$-axes oriented grains. The formation of a predominant (001) orientation is thought to be driven by its low surface energy on the (001) plane of Nb:SrTiO$_3$.

### 3.2 Preferred orientation of BNdT films on Nb:SrTiO$_3$(011)

Figures 3(a) and (b) show the XRD $\theta$–$2\theta$ scan and pole figure (recorded from the BNdT 117 reflection) of the BNdT film on Nb:SrTiO$_3$(011), respectively. In Fig. 3(a), the 200/020/119 diffraction peak is much stronger than the 117 peak, suggesting that the film is predominantly 100/010- and 119-oriented. The crystallographic orientation of the film was confirmed by the X-ray pole figure in Fig. 3(b). The pole figure consists of two sets of peaks marked with “A” and “B”, respectively. The major set “A” includes four peaks appearing at $\psi \approx 57^\circ$ and stems from the 100/010-oriented BNdT grains because of the angles $\angle(100):(117) = 56.88^\circ$ and $\angle(010):(117) = 56.7^\circ$, while the minor set “B” is composed of peaks located at $\psi \approx 7^\circ$, 63$^\circ$ and 86$^\circ$ and originates from the 119-oriented grains [cf. the angles $\angle(119):(117) = 7.16^\circ$, $\angle(119):(117) = 62.89^\circ$, $\angle(119):(117) = 85.6^\circ$]. The background intensities of the pole figure are in the range of 10–50 cps, while the maximum intensity of the peaks at $\psi \approx 57^\circ$ is about 6760 cps, indicating a mixture of (100)/(010), (119) and random orientations. According to the pole figure, the volume fraction of the (100)/(010)-oriented grains in the film can be estimated to be around 30%, while that of the 119-oriented grains to be ~18%.

Figure 4 shows a cross-sectional TEM image of the BNdT film grown on Nb:SrTiO$_3$(011). One can see that the 430 nm thick film consists of columnar grains of 100–200 nm in lateral size. Selected area electron diffraction (SAED) investigations indicate that the columnar grains 1–5 are $a/b$-axes oriented. For instance, the inset of Fig. 4 shows a SAED pattern of the columnar grain 2. The pattern could result from the [100] zone or from the superposition of [010] and [110] zones, where the [010] zone...
3.3 Ferroelectric anisotropy of BNdT films

Since the spontaneous polarization \( P \) in BNdT is directed almost along the \( a \)-axis, the \( P \), vector of (001)-, (119)- and (100)-oriented BNdT films tilt away from the film growth direction by \( \sim 90^\circ \), \( \sim 46^\circ \), and \( \sim 0^\circ \), respectively [cf. the angles \( \angle (001):(100) = 90^\circ \), \( \angle (119):(100) = 46.4^\circ \), and \( \angle (100):(100) = 0^\circ \)]. The perpendicular polarization components of BNdT films having different orientations can be estimated by means of the above angles, as schematically shown in Fig. 5. For (001), (119), and (100) orientations, the polarization components perpendicular to the film surface are proportional to the values of \( P_{\perp}^{(001)} = |P| \cdot \cos 90^\circ = 0 \), \( P_{\perp}^{(119)} = |P| \cdot \cos 46^\circ \approx 0.7|P| \), and \( P_{\perp}^{(100)} = |P| \cdot \cos 0^\circ = |P| \), respectively. Accordingly, the non-\( c \)-axis oriented BNdT film is expected to exhibit a high \( 2P_c \) value in planar-type capacitors while the \( 2P_c \) value of the \( c \)-axis-oriented BNdT film is rather low or close to zero.
where $2P_{\text{c-axis}}$, $2P_{\text{a-b-axis}}$, $2P_{\text{c-axis}}$, and $2P_{\text{random}}$ denote the $2P_0$ values of BNdT thin films with pure c-axis, pure a/b-axes, pure (119), and complete random orientations, respectively. Since $2P_{\text{c-axis}} = 0$, we know $2P_{\text{random}} \approx 7.0 \, \mu\text{C/cm}^2$ from Eq. (1). Since $P_{\text{a-b-axis}}^{(00)} \approx 0.7 \times P_{\text{a-b-axis}}^{(119)}$, so $2P_{\text{a-b-axis}} \approx 0.7 \times 2P_{\text{a-b-axis}}^{(119)}$. Then we can obtain $2P_{\text{a-b-axis}} \approx 58.2 \, \mu\text{C/cm}^2$ according to Eq. (2).

The estimated $2P_0$ value of $\approx 58.2 \, \mu\text{C/cm}^2$ for the BNdT film with pure a/b-axes orientation is a little lower than the $2P_0$ (64 $\mu\text{C/cm}^2$) for the a/b-axes-oriented BLT epitaxial films grown by PLD on SrRuO$_3$/YSZ/Si substrate [3]. The $2P_0$ value of the predominantly c-axis-oriented BNdT film is quite lower than that of the film with predominant 100/010/119 orientations. This fact confirms that the spontaneous polarization vector of BNdT is closer to the a-axis rather than the c-axis, such as the cases in BLT and Bi$_4$Ti$_3$O$_{12}$.

4 Conclusions Ferroelectric BNdT thin films were deposited on Nb-doped SrTiO$_3$, single crystals through a sol–gel process. The films grown on Nb: SrTiO$_3$(011) are of predominant 100/010/119 orientations and are composed of columnar grains penetrating the film thickness. While the films on Nb: SrTiO$_3$(001) have predominant c-axis orientation and consist of prolate grains. The former films showed a $2P_0$ value of $\approx 28.4 \, \mu\text{C/cm}^2$, and a $2P_0$ of $\approx 5.7 \, \mu\text{C/cm}^2$ was obtained in the latter films. The anisotropic ferroelectric properties support those findings that the major polarization direction in BNdT lies along the a-axis. Besides the orientation of SrTiO$_3$ substrates, heating rapidly for crystallization is crucial for the nucleation of non-c-axis oriented grains.

Acknowledgement This work was supported by the Program for New Century Excellent Talents (NCET) in University, the Research Foundation of Ph.D-degree-conferred subject in University (20070512002), the Program for Excellent Young Scientists in Wuhan City, China, and the Open Project Program of the Key Laboratory of Ministry of Education on Low Dimensional Materials and Application Technology, Xiangtan University, China (KF0606); work at MPI Halle supported by DFG via SFB 418 and FOR 404.

References