Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Crystal Growth 271 (2004) 50–54

JOURNAL OF CRYSTAL GROWTH

www.elsevier.com/locate/jcrysgro

Growth of epitaxially twinned ferroelectric $Bi_{3.25}La_{0.75}Ti_3O_{12}(0\,2\,8)$ thin film on GaN substrate

Jae-Yeol Hwang[a], Chae-Ryong Cho[a,*], Se-Young Jeong[b]

[a]*Nano-Surface Analysis Team, Korea Basic Science Institute, Busan 609-735, Korea*
[b]*Division of Nano-Science and Technology, Pusan National University, Busan 609-735, Korea*

Received 25 February 2004; accepted 12 July 2004
Communicated by M. Kawasaki
Available online 8 September 2004

Abstract

Epitaxially twinned (0 2 8)-oriented $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) thin films were grown on GaN(0 0 2)/Al_2O_3 (0 0 0 6) substrates by pulsed laser deposition. The BLT layer deposited on GaN substrate showed sixfold-like symmetric peaks in a ϕ scan of (0 0 6) reflection and 12 peaks in that of the (1 1 7) reflection. In order to investigate hetero-epitaxial growth, origin of six and 12 peaks in the ϕ scan, and the domain structure of the BLT thin film, the X-ray analysis including θ–2θ, ω, ϕ scan, and pole figure measurement were performed. The hetero-epitaxial growth was studied by atomic arrangements and domain distribution with calculated lattice mismatch, interplanar angles, and atomic distances.

PACS: 68.55.–a; 81.15.–z; 73.40.Qv; 85.50.–n

Keywords: A1. MFS-structure; A1. Twin; A3. Epitaxy; A3. Thin-film growth; B1. BLT; B1. GaN; B2. Ferroelectric materials

---

1. Introduction

La-substituted $Bi_4Ti_3O_{12}$, especially $Bi_{3.25}La_{0.75}Ti_3O_{12}$, film has attracted much attention because of good fatigue endurance, low deposition temperature, and therefore their potential application to ferroelectric random access memories [1,2]. Since most of these materials have highly anisotropic physical properties, and since some applications, such as waveguide and electro-optic (EO) devices, require oxide thin films with unique and preferred crystalline orientations, a strong emphasis has been placed on epitaxial growth [3]. Although reports on the epitaxial growth of

---

*Corresponding author. Korea Basic Science Institute, Busan branch, Pusan National University Campus, Busan 609735, Republic of Korea. Tel.: +82-51-510-3266; fax: +82-51-582-1231.

E-mail addresses: wolfhhh@pnu.edu (J.-Y. Hwang), crcho@kbsi.re.kr (C.-R. Cho).

0022-0248/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jcrysgro.2004.07.020

$Bi_4Ti_3O_{12}$ (BTO) and BLT films have been published, most of them are concerned with *c*-axis oriented films and films on insulating single crystal substrates used in optical applications [4–6]. Ferroelectric BTO is a highly anisotropic pseudo-orthorhombic structure with $a = 5.45\,\text{Å}$, $b = 5.41\,\text{Å}$, and $c = 32.83\,\text{Å}$ at room temperature. Bismuth-layered perovskite films with *c*-axis orientation do not have a polarization component along the film normal. Because the major component of the spontaneous polarization of BTO is directed along its *a*-axis [7,8], the growth of non-*c*-axis-oriented films is required to achieve a higher polarization component along the normal to the film plane. The unstability of Si makes serious problems [9–11], such as interdiffusion between ferroelectric layer and Si substrate, degradation of the ferroelectric properties, and increase of the leakage current in Si-based ferroelectric films. It is very difficult to fabricate the epitaxial ferroelectric thin film on the Si substrate without any oxide buffer layer. GaN has high temperature and chemical stability, good mobility, and (optical) direct band gap. These are suitable for high speed devices and opto-electronic applications. However, there has been few reports on the growth of metal–ferroelectric–semiconductor (MFS) stacked thin films using GaN as a semiconductor substrate [12,13]. In this letter, we report in detail on the epitaxial growth and structural analysis of the BLT on a GaN(0 0 2)/Al_2O_3 (0 0 0 6) substrate prepared by the pulsed laser deposition (PLD) technique.

2. Experimental procedure

The GaN layer on Al_2O_3 substrate as a semiconductor and bottom electrode is prepared by metal-organic chemical vapor deposition (MOCVD) technique. In order to increase carrier concentration and mobility, we artificially doped Si into the GaN layer under MOCVD process. The thickness of Si-doped n-type GaN epi-layer was 2 μm. The carrier concentration and mobility of the Si-doped GaN layer were $1 \times 10^{18}\,\text{cm}^{-3}$ and $150\,\text{cm}^2/\text{V}\cdot\text{s}$, respectively. A BLT layer was deposited on the GaN(0 0 2) epitaxial layer by PLD using a KrF excimer laser (248 nm) with a fluence of $5\,\text{J}/\text{cm}^2$ operating at a repetition rate of 20 Hz. The substrate temperature was maintained at 700 °C and the partial pressure of O_2 was varied from 100 to 300 mTorr. The distance between target and substrate was 5 cm. The domain structure, their orientations, and epitaxial growth of BLT thin film were determined by X-ray diffraction (XRD, Philips X'Pert Pro) using monochromatized Cu-Kα_1 radiation with ω rocking curve, ϕ scan, and pole figure modes. For the electrical characterizations, gold top electrode $2 \times 10^{-3}\,\text{cm}^2$ in size, was sputter-deposited at room temperature with a shadow mask. Dielectric properties and leakage current characteristics of the film were determined by a HP 4294A high precision impedence analyzer and a Keithley 6517A electrometer with a DC voltage-stepping mode (step: 0.01 V).

3. Results and discussion

Fig. 1 shows the surface topographies of the BLT thin film on the GaN substrate investigated by atomic force microscope (AFM). As-deposited films were crack-free, uniform, transparent, dense, and good adhesion to the substrates. The thickness of the BLT film was estimated to be 0.6 μm by cross-section image of scanning electron microscope (SEM). As shown in Fig. 2, the BLT thin film deposited on GaN/Al_2O_3 substrate at 700 °C has single-phase without any secondary phase, such as BiO_x, Bi–Ti–O compounds, and non-ferroelectric fluorite and pyrochlore phase. The full-width at half-maximum (FWHM) values of

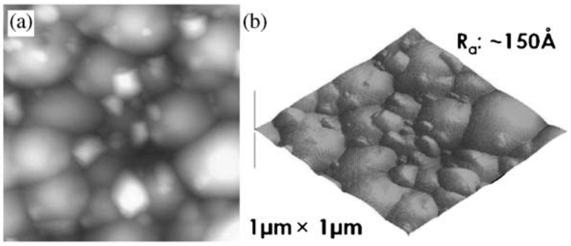

Fig. 1. Surface (a) image and (b) topography of (0 2 8)-oriented BLT thin film on GaN/Al_2O_3 substrate by AFM measurement.

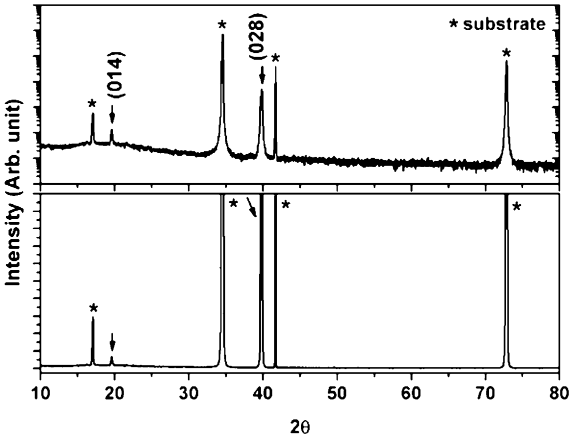

Fig. 2. Gonio scan result of BLT thin film on GaN/Al_2O_3 substrate (top: log scale plot, bottom: linear scale plot).

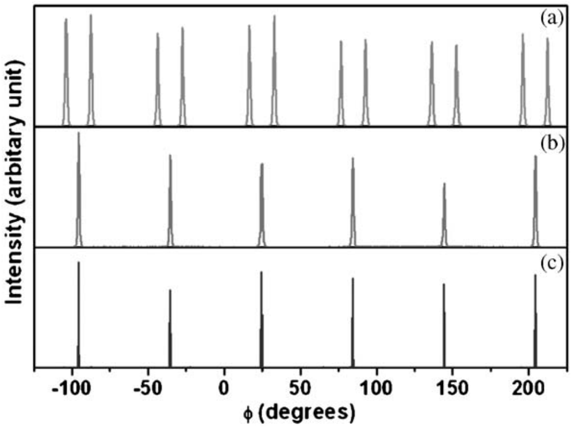

Fig. 3. The ϕ scans of (a) (1 1 7), (b) (0 0 6) in (0 2 8)-oriented BLT thin film, and (c) (1 0 2) reflections in (0 0 2)-oriented GaN substrate.

BLT (0 2 8) and GaN (0 0 2) reflections were 0.93° and 0.11° in ω scans, respectively. Fig. 3 shows ϕ scans of the BLT (1 1 7), (0 0 6), and GaN (1 0 2) reflection, which were obtained under the fixed condition of $\psi = 36.182°$ ($2\theta = 30.062°$), $\psi = 56.60°$ ($2\theta = 16.19°$), and $\psi = 43.19°$ ($2\theta = 48.10°$), respectively. In a ϕ scan of the BLT (0 0 6) reflection [Fig. 3(b)], the sixfold-like symmetric peaks indicate the specific in-plane-epitaxial growth pattern of the BLT(0 2 8) film on GaN(0 0 2) substrate. The preferential growth of the (0 2 8)-oriented BLT/GaN/Al_2O_3 hetero-structure can be understood in Figs. 4 and 5.

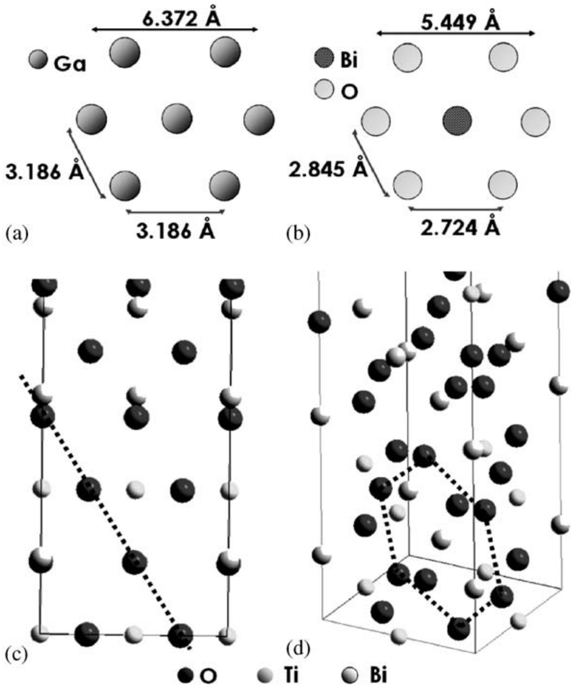

Fig. 4. Atomic arrangements of (a) Ga ions on GaN(0 0 2) plane and (b) oxygen ions on BLT(0 2 8) plane. The (c) (1 0 0) view and (d) (1 1 1) view of simulated BLT unit cell. (dashed lines indicate BLT (0 2 8) plane.)

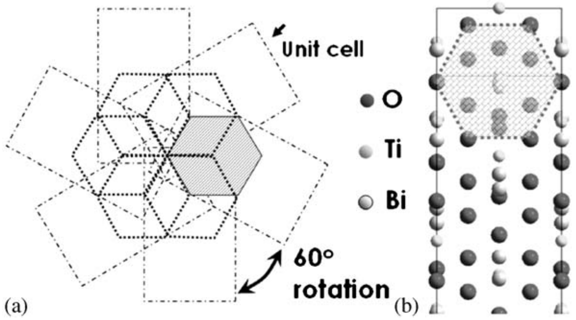

Fig. 5. (a) Top view of six (possible) azimuthal domains of (0 2 8)-oriented BLT thin film on GaN substrate. The six rectangles with dashed or dotted line means unit cell of (0 2 8)-oriented BLT. (b) Simulated unit cell of BLT. The hexagon means that the distribution of oxygen ions (Fig. 4(b)) on BLT (0 2 8) plane.

The atomic distance between Ga (or N) atoms on the GaN (0 0 2) plane (3.186 Å), is close to that between oxygen atoms on the BLT (0 2 8) plane (2.845 Å). The lattice misfit is 10% which was

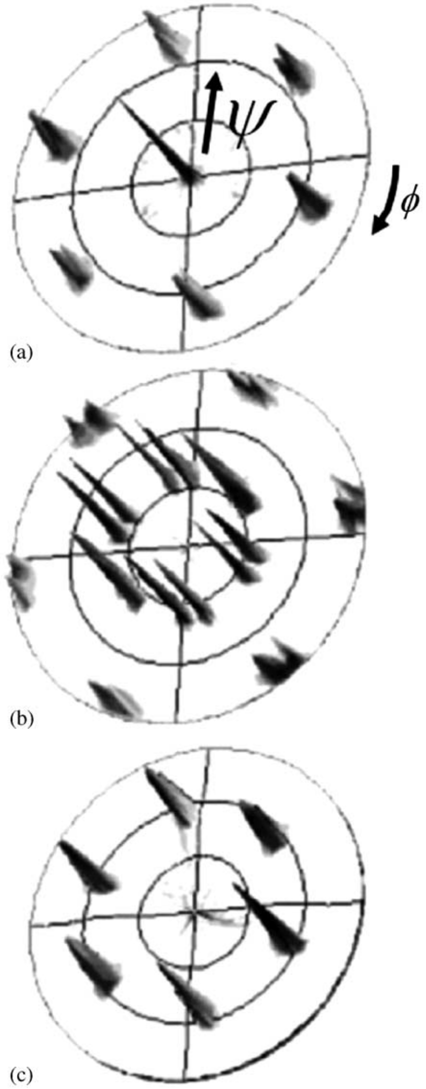

Fig. 6. X-ray pole figures of (0 2 8)-oriented BLT thin film on GaN(0 0 2)/Al_2O_3 (0 0 0 6) substrate. The fixed 2θ angles were (a) 39.889°, (b) 30.062°, and (c) 16.193°, which correspond to the BLT (0 2 8), (1 1 7), and (0 0 6) reflections, respectively.

calculated by the $(d_{\text{film}}\text{-}d_{\text{sub}})/d_{\text{sub}}$ relation. But, The extended atomic distance mismatch (EADM) [14] for large lattice mismatch epitaxial growth is only 0.78%. The eight times the Ga–Ga (or N–N) distance on GaN (0 0 2) plane is nearly equal to nine times the O–O distance on BLT (0 2 8) plane.

Table 1
Calculated Bragg reflection angles of (0 2 8)-oriented BLT thin film

Bragg reflection	2θ	ψ
(0 2 8)	39.899°	0°
(2 0 8)	39.683°	72.27°
(0 0 6)	16.193°	56.60°
$(1\,1\,7)/(\bar{1}\,1\,7)$	30.062°	36.18°
$(\bar{1}\,\bar{1}\,7)/(\bar{1}\,1\,\bar{7})$	30.062°	83.71°

Due to the sixfold symmetry of the Ga (or N) networks on the GaN(0 0 2) plane, there are six possible ways (Fig. 5(a)) in which the axes perpendicular to (0 2 8) plane of BLT thin film can be aligned. The six symmetric peak positions of the BLT (0 0 6) reflection (Fig. 3(b)) in ϕ scan are almost coincident to those of the GaN (0 0 2) reflection (Fig. 3(c)). This means that the overgrown BLT layer was azimuthally oriented to the GaN substrate following the near coincidence site lattice with a 60° rotation (Fig. 5(a)).

The pole figure (in square-root scale) in Fig. 6(c) shows that all of the six possible ways of growth occur. As shown in Fig. 6(a), the ψ angle between the (0 2 8) and (2 0 8) plane is 72.266°. The pole in Fig. 6(a) at $\psi = 0°$ is the (0 2 8) reflection, and the six peaks at $\psi = 72.2°$ are the (2 0 8) reflection of the BLT thin film. The ψ reflection angles of all pole figure scans agreed with the calculation in Table 1. Because of the diffraction geometry of (0 2 8)-oriented BLT thin film, a pole figure scan of BLT (0 0 6) reflection (Fig. 6(c)) showed six diffraction peaks. But, a pole figure scan of the BLT (1 1 7) reflection (Fig. 6(b)) showed two sets of twinned sixfold-like symmetric peaks, which consisted of twelve peaks of (1 1 7) and $(\bar{1}\,1\,7)$ reflections at $\psi = 36.18°$, and twelve peaks of $(\bar{1}\,\bar{1}\,7)$ and $(\bar{1}\,1\,\bar{7})$ reflections at $\psi = 83.71°$. These showed that BLT/GaN thin film has two domains (a–b twins), which coincides with the possible number of domain due to the tetragonal-to-orthorhombic (TO) transformation [15], in each azimuthal domain.The FWHM value of the BLT (0 2 8) plane is relatively high due to the twins and sixfold like azimuthal domains, but that of the GaN is very low. Twinning relieves the biaxial stress in the basal plane of the TO transformation. When the substrate crystal has a higher symmetry than that of the overgrown film, a finite number of differently oriented island–nuclei develop, which ensures a finite number of misorientations across boundaries in the film. Differently oriented island–nuclei form to minimize interfacial energy by maximizing the lattice coincidence according to the near coincidence site lattice (NCSL) model [15–17] and minimizing the misfit and strain energy across the film/substrate interface.

4. Conclusions

In summary, non-*c*-axis-oriented epitaxially twinned $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin film was successfully grown on GaN(0 0 2)/Al_2O_3 substrates by pulsed laser deposition. Due to the structure of the GaN substrate and large lattice misfit between the BLT(0 2 8) layer and the GaN(0 0 2) substrate, six-possible ways of growth occurred and the BLT layer deposited on the GaN substrate has a-b twins. These were confirmed by ϕ scans and pole figure measurements with lattice calculations. The BLT/GaN thin film showed good leakage current characteristics ($1.1 \times 10^{-9}\,A/cm^2$ at 150 kV/cm), low dielectric loss (0.8% at 100 kHz), and high dielectric constant (215 at 100 kHz).

Acknowledgements

This work was supported by a Grant No. R01-2003-000-10027-0 from the Korea Science and Engineering Foundation.

References

[1] A. Kingon, Nature (London) 401 (1999) 658.
[2] B.H. Park, B.S. Kang, S.D. Bu, T.W. Noh, J. Lee, W. Jo, Nature (London) 401 (1999) 682.
[3] R. Ramesh, D.G. Scholem, Science 296 (2002) 1975.
[4] H.N. Lee, D. Hesse, Appl. Phys. Lett. 80 (2002) 1040.
[5] W. Jo, T.W. Noh, Appl. Phys. Lett. 65 (1994) 2780.
[6] R. Ramesh, A. Inam, B. Wilkens, W.K. Chan, T. Sands, D.K. Fork, T.H. Geballe, J. Evans, J. Bullington, Appl. Phys. Lett. 59 (1991) 1782.
[7] S.E. Cummins, L.E. Cross, J. Appl. Phys. 39 (1968) 2268.
[8] H.N. Lee, D. Hesse, N. Zakharow, U. Gosële, Science 296 (2002) 2006.
[9] S.Y. Chen, C.L. Sun, S.B. Chen, A. Chin, Appl. Phys. Lett. 80 (2002) 3168.
[10] S.W. Wang, W. Lu, X.S. Chen, N. Dai, X.C. Shen, H. Wang, M. Wang, Appl. Phys. Lett. 81 (2002) 111.
[11] Y. Hou, X.H. Xu, H. Wang, M. Wang, S.X. Shang, Appl. Phys. Lett. 78 (2001) 1733.
[12] W.P. Li, R. Zhang, Y.G. Zhou, J. Yin, H.M. Bu, Z.Y. Luo, B. Shen, Y. Shi, Z.C. Huang, Appl. Phys. Lett. 75 (1999) 2416.
[13] V. Fuflyigin, A. Osinsky, F. Wang, P. Vakhutinsky, P. Norris, Appl. Phys. Lett. 76 (2000) 1612.
[14] C.J. Sun, P. Kung, A. Saxier, H. Ohsato, K. Haritos, M. Razeghi, J. Appl. Phys. 75 (1994) 3964.
[15] J. Sapriel, Phys. Rev. B 12 (1975) 5128.
[16] R.W. Balluffi, A. Brokman, A.H. King, Acta Metall. 30 (1982) 1453.
[17] A. Trampert, K.H. Ploog, Cryst. Res. Technol. 35 (2000) 793.