Materials Letters 193 (2017) 240–243

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

High-performance $BiFe_{0.95}Mn_{0.05}O_3$ ferroelectric film epitaxially integrated on GaN substrate with LSMO/TiO_2 bi-layer buffer

Leilei Xu [a,b], Xiaomin Li [a,*], Qiuxiang Zhu [a], Xiaoke Xu [a,c], Meng Qin [a,b]

[a] State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, No. 1295 Dingxi Road, Shanghai 200050, PR China
[b] University of Chinese Academy of Sciences, No. 19A Yuquan Road, Beijing 100049, PR China
[c] School of Materials Science and Engineering, Shanghai Institute of Technology, No. 100 Haiquan Road, Shanghai 201418, PR China

ARTICLE INFO

Article history:
Received 10 November 2016
Received in revised form 17 January 2017
Accepted 25 January 2017
Available online 27 January 2017

Keywords:
Ferroelectrics
Bismuth ferrite
Bi-layer buffer
Epitaxial growth
GaN integration

ABSTRACT

The highly (111)-oriented $BiFe_{0.95}Mn_{0.05}O_3$ (BFMO) films owning excellent ferroelectric performance have been epitaxially grown on (0002) GaN substrates with $La_{0.7}Sr_{0.3}MnO_3$ (LSMO)/TiO_2 bi-layer buffer by pulsed laser deposition. By means of the LSMO/TiO_2 bi-layer buffer, the lattice mismatch between perovskite (111) BFMO and wurtzite (0002) GaN was miraculously decreased from 12.4% to 1.4%. The remnant ferroelectric polarization and coercive field of the BFMO (111) film were determined to be 115 μC/cm^2 and 450 kV/cm, respectively. Compared with the BFMO film deposited on the bare GaN substrate, the remnant ferroelectric polarization was enhanced by 92%. The piezoresponse force microscopy (PFM) image further confirmed that the BFMO (111) film owned perfect ferroelectric switching properties.

1. Introduction

The integration of ferroelectric film with wide band-gap semiconductor has been intensively investigated due to its wide application in power electronics, smart sensor system and ferroelectric field-effect transistors (FFET) [1–3]. Recently, the third generation semiconductor GaN has attracted intensive concern due to its distinct advantages of wider band gap, high-saturated electron drift velocity and high operating temperature. However, there is much less research on integration of ferroelectric film with GaN-base semiconductor, and the ferroelectrics involve only a few traditional ferroelectric materials, such as BST [1], PZT [2], and $LiNbO_3$ [4].

As the only single-phase multiferroic material at room temperature, bismuth ferrite (BFO) has attracted considerable attention, owing to its promising physics about large remnant ferroelectric polarization and high Curie temperature (Tc = 1103 K), which make it be the promising candidate gate material for GaN-base FFET devices [5,6]. Meantime, to enhance the material properties and device performance, it is desirable to achieve (111)-oriented BFO film in that the spontaneous polarization of bulk BFO lies along the (111) axis [7]. Moreover, to reduce the large leakage current of BFO film, 5%Mn-doped $BiFe_{0.95}Mn_{0.05}O_3$ (BFMO) was usually used [8]. Thus, we expected to realize the growth of (111)-oriented $BiFe_{0.95}Mn_{0.05}O_3$ film on GaN substrate. Nevertheless, epitaxial growth of perovskite BFMO (111) film on wurtzite GaN (0002) substrate meets a huge obstacle due to the large lattice mismatch. Therefore, it is imperative to introduce an appropriate buffer layer between BFMO and GaN, which can promote the epitaxial growth of BFMO films.

In this study, we have realized the epitaxial growth of highly (111)-oriented BFMO (111) films on GaN (0002) substrates by incorporating the LSMO/TiO_2 bi-layer buffer. The effects of the LSMO/TiO_2 layer on the crystallinity, surface morphology and ferroelectric properties of BFMO were also discussed.

2. Experimental

In this work, (111) LSMO/(100) TiO_2 buffer layers and 5%Mn-doped $BiFe_{0.95}Mn_{0.05}O_3$ (BFMO) films were epitaxially grown on the 2-μm thick (0002) GaN samples prepared on c-sapphire substrates by pulsed laser deposition (PLD) using a KrF excimer laser (λ = 248 nm). Firstly, the TiO_2 buffer layer was deposited on bare GaN substrate at a temperature of 550 °C and oxygen pressure of 1×10^{-5} Pa with the laser energy density and the repeat frequency of 3 J/cm^2, 1 Hz, respectively. Then, the LSMO buffer layer was deposited on TiO_2 buffer layer at a temperature of 750 °C and oxygen pressure of 30 Pa with the laser energy density and the repeat

* Corresponding author.
E-mail address: lixm@mail.sic.ac.cn (X. Li).

http://dx.doi.org/10.1016/j.matlet.2017.01.125
0167-577X/

frequency of 3 J/cm^2, 2 Hz, respectively. Finally, BFMO films were then grown on LSMO/TiO_2 buffered GaN at a temperature of 680 °C and oxygen pressure of 15 Pa with the laser energy density and the repeat frequency of 3 J/cm^2, 5 Hz, respectively. The surface morphology was studied by atomic force microscope (Nanocute SII, Seiko, Japan). The phase purity, crystallinity, epitaxial properties were characterized *in situ* by reflection high-energy electron diffraction (RHEED) during PLD and *ex situ* by high resolution Bruker D8 Discover X-ray diffractometer, equipped with a 4-bounce Ge (2 2 0) monochromator and Cu Kα radiation (λ = 0.15406 nm), respectively. Cross-sectional transmission electron microscopy images and selected area electron diffraction patterns were obtained on a Tecnai G2 F20 transmission electron microscopy (TEM).

In order to form a plate capacitor for electric measurements of BFMO films, circular Ag top electrodes of ∼100 μm diameter were deposited by magnetron sputtering on the surface of BFMO films through a shadow mask. Polarization-electric-field (P-E) hysteresis curves and leakage currents of BFMO films were characterized by Precision Multiferroic Analyzer (Radiant Technologies, Inc. USA).

3. Results and discussion

Fig. 1 shows the XRD patterns of the BFMO films deposited on bare GaN and LSMO/TiO_2 buffered GaN, respectively. It can be obtained from Fig. 1(a) that the BFMO films showed (1 0 0), (1 0 1), and (2 0 0) peaks of perovskite phase, indicating that the BFMO films deposited directly on GaN were poly-crystalline. However, with LSMO/TiO_2 buffer layers, the BFMO films showed purely (1 1 1) diffraction peak, demonstrating that the BFMO films were of single phase and highly (1 1 1)-oriented. XRD rocking curve taken on the BFMO (1 1 1) diffraction peak had a full width at half maximum of 0.37° ((1) inset of Fig. 1(b)). The inset (2) of Fig. 1(b) showed the RHEED patterns monitored *in situ* during the deposition process of each layer. Both the bare GaN-on-sapphire substrate and TiO_2 buffer layer diffraction pattern showed clear bright streaks, indicating that the surface of GaN and TiO_2 were smooth and well periodic. Besides, several Bragg-reflection spots superpose on sharp streak. It means that the LSMO film was grown in the Stranski-Krastanov growth mode. And the BFMO diffraction pattern was spotty, implying three-dimension growth. The XRD ϕ scans of BFMO (1 0 1) and GaN (1 0 −1 1) diffraction peaks were shown in Fig. 1(c). It can be find that sixfold symmetrical diffraction peaks appear 60° separate from each other for both the BFMO and GaN films, indicating the BFMO films were epitaxially grown on the GaN substrates. Furthermore, the presence of 1 0 1 reflections every 60° in XRD ϕ-scan pattern results from the BFMO film twinning in the growth plane by a 180° in-plane rotation [9]. According to the relative position of the BFMO(1 0 1) (2θ = 22.49°, χ = 35.26°) and GaN(1 0 −1 1)(2θ = 36.96°, χ = 61.61°), we can get that the in-plane orientation relationship was (1 1 1) × <1 1 0>BFMO//(0 0 0 2) × <1 1 −2 0>GaN. AFM image revealed that the (1 1 1) BFMO film had a flat surface with a root-mean-square roughness of 3.57 nm, as shown in Fig. 1(d).

Cross-sectional transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were conducted to characterize the BFMO/LSMO/TiO_2/GaN heterostructure. The thicknesses of the BFMO, LSMO and TiO_2 layer were 241 nm, 8 nm and 2 nm, respectively, as shown in Fig. 2(a). Besides, the interfaces of different layers are sharp, obtained from a representative cross-sectional HRTEM image (Fig. 2(b)). The selected area electron diffraction (SAED) pattern of the LSMO/TiO_2/GaN heterostructure along the [1 1 −2 0] direction of the GaN substrate was shown in Fig. 2(c). A superimposition of one [1 1 −2 0] zone axis SAED pattern of GaN (indicated by a red dashed rectangle), one [0 0 1] zone axis SAED pattern of TiO_2 (indicated by

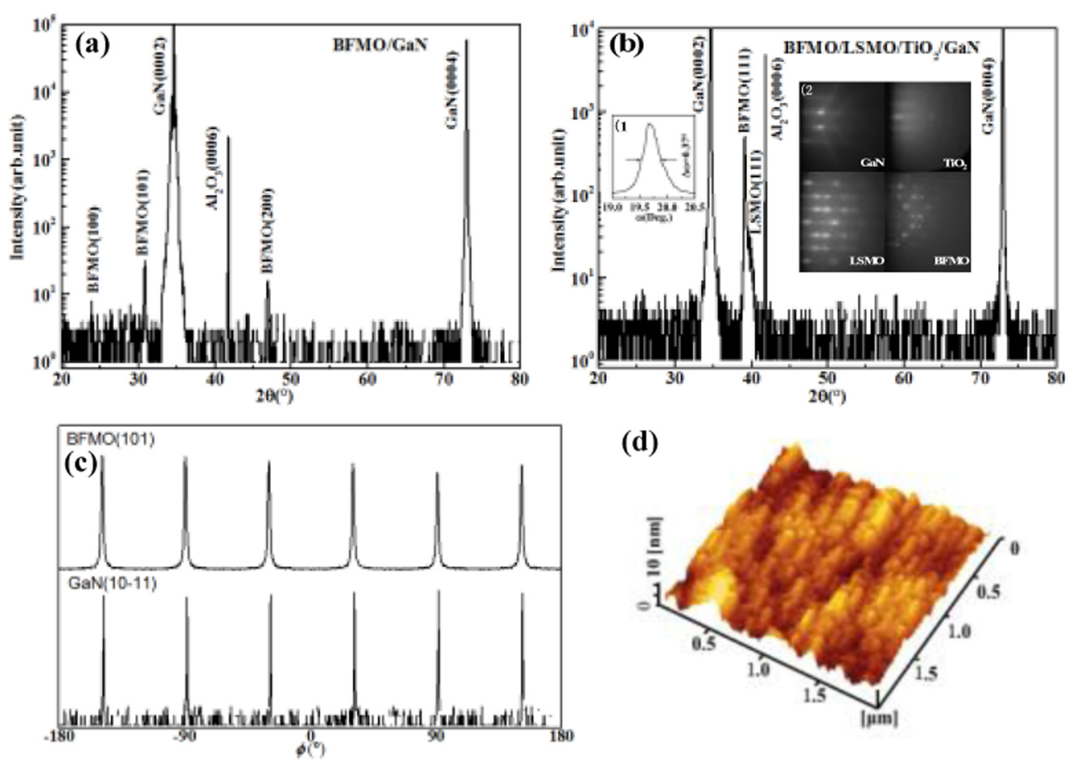

Fig. 1. XRD θ-2θ scan pattern of BFMO films deposited on (a) bare GaN and (b) LSMO/TiO_2 buffered GaN; (inset (1)) rocking curve of the (1 1 1) BFMO diffraction peak, (inset (2)) RHEED patterns of GaN, TiO_2, LSMO and BFMO layer. (c) XRD ϕ-scan patterns taken on the BFMO (1 0 1) and GaN (1 0 −1 1) diffraction peaks, respectively. (d) AFM image of the BFMO (1 1 1) film.