



## Letter

Atomic structures of planar defects in 0.95(Na<sub>0.5</sub>Bi<sub>0.5</sub>)TiO<sub>3</sub>–0.05BaTiO<sub>3</sub> lead-free piezoelectric thin filmsShao-Bo Mi<sup>a,b,\*</sup>, Xiao-Wei Jin<sup>a</sup>, Sheng Cheng<sup>a</sup>, Ming Liu<sup>a</sup>, Lu Lu<sup>a</sup>, Chun-Lin Jia<sup>a,c</sup><sup>a</sup> International Center for Dielectric Research, The School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an 710049, PR China<sup>b</sup> State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, PR China<sup>c</sup> Peter Grünberg Institute and Ernst Ruska Center for Microscopy and Spectroscopy with Electrons, Forschungszentrum Jülich, D-52425 Jülich, Germany

## ARTICLE INFO

## Article history:

Received 12 December 2014

Received in revised form 9 February 2015

Accepted 22 February 2015

Available online 26 February 2015

## Keywords:

Piezoelectric film

Planar defect

Microstructure

Scanning transmission electron microscopy

## ABSTRACT

Two types of planar defects are found in 0.95(Na<sub>0.5</sub>Bi<sub>0.5</sub>)TiO<sub>3</sub>–0.05BaTiO<sub>3</sub> lead-free piezoelectric thin films prepared on polycrystalline Ni metal substrates. The atomic structures of these defects are characterized by means of aberration-corrected scanning transmission electron microscopy. The first type of planar defects is related to the (Bi<sub>2</sub>O<sub>2</sub>)<sup>2+</sup> layers parallel to (100) plane of thin films. The second type of planar defects is determined as complex planar defects made up of edge-sharing TiO<sub>6</sub> octahedra with the Bi cations residing in the cavities formed by the octahedral network. The formation of the Bi-rich defects is believed to affect the physical properties of the thin films.

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## 1. Introduction

In recent years, lead-free piezoelectric materials of sodium bismuth titanate (NBT)-based materials, in particular, (1-x)(Na<sub>0.5</sub>Bi<sub>0.5</sub>)TiO<sub>3</sub>-xBaTiO<sub>3</sub> (NBT-BT) solid solutions, have attracted considerable attention since they exhibit promising piezoelectric properties, showing great potential of applications in transducers and other electromechanical devices [1–3]. With the continued scaling to nanoelectromechanical systems (NEMS), thin films of NBT-based materials have been fabricated as promising lead-free alternative piezoelectrics by various deposition techniques, such as pulsed laser deposition, metal-organic decomposition and solid-state reaction [4–6]. The dielectric and piezoelectric properties of the films can be strongly modulated by the microstructure of the films, such as structural defect, grain boundary and chemical inhomogeneity. Indeed, the properties of piezoelectric NBT-BT films usually deviate from the bulk counterpart, e.g. high leakage current density [7]. Also, it has been reported that non-stoichiometric compositions deviated from (Na<sub>0.5</sub>Bi<sub>0.5</sub>)TiO<sub>3</sub>, e.g. Bi-deficient/Na-excess compositions of (Na<sub>0.5+x</sub>Bi<sub>0.5-x</sub>)TiO<sub>3+x</sub>, resulted in dramatically deteriorated ferroelectric properties and were unable to be poled to induce piezoelectric functions [8]. To

date, the origins producing the property deviation remain unclear due to lack of microstructure information of the piezoelectric NBT-BT films.

Recently, excellent electromechanical properties and low dielectric loss were obtained for 0.95(Na<sub>0.5</sub>Bi<sub>0.5</sub>)TiO<sub>3</sub>-0.05BaTiO<sub>3</sub> (0.95NBT-0.05BT) single crystal with rhombohedral structure [9]. The fabrication of piezoelectric 0.95NBT-0.05BT films on Ni polycrystalline substrates is a potential candidate for the development of the piezoelectric wafer active sensor arrays for structural health monitoring [10]. In this work, the structural properties of lead-free piezoelectric 0.95NBT-0.05BT films on Ni substrates buffered by a NiO layer were studied by means of high-resolution high-angle annular dark field (HAADF) imaging [11] combined with annular bright-field (ABF) imaging [12] in aberration-corrected high-resolution scanning transmission electron microscopy (STEM).

## 2. Experimental

The 0.95NBT-0.05BT films were fabricated on polycrystalline Ni foil using the high-pressure sputtering system. The flowing pressure was 0.2 mbar with the mixed ambient of Ar and O<sub>2</sub> at the ratio of 1:1. Under the film growth conditions, a NiO buffer layer unavoidably forms between the 0.95NBT-0.05BT films and Ni foil. To minimize oxidation of Ni, a two-step method was applied to grow the 0.95NBT-0.05BT films on Ni metal substrates. Details of the film growth were given elsewhere [10].

Cross-sectional specimens for electron microscopy investigation were prepared by focused ion beam (FIB) method [13] in a scanning electron microscope dual beam (FEI Helios600i FIB/SEM). Atomic-resolution HAADF and ABF investigations were performed on a JEOL ARM 200F with a probe aberration corrector, operated at 200 kV. In STEM mode a probe size of 0.1 nm and convergence angle of

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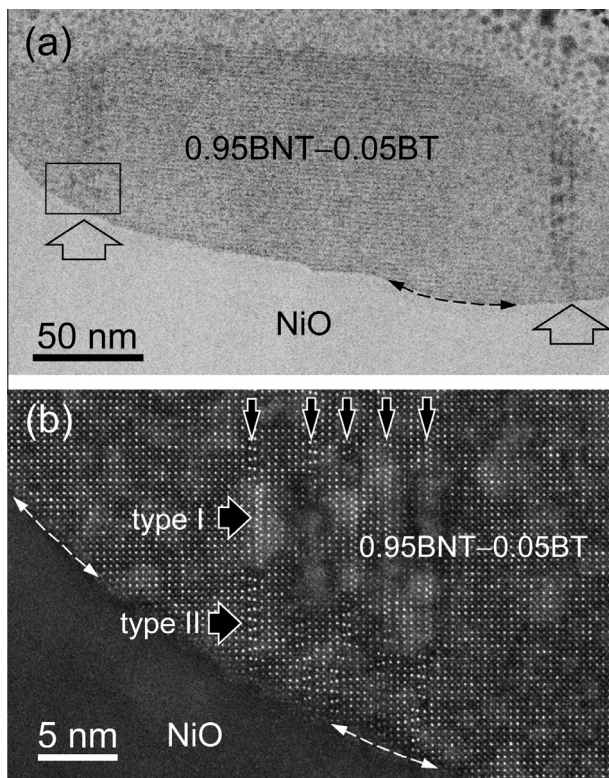
$\alpha = 22$  mrad were used for HAADF and ABF imaging experiments. The HAADF and ABF detectors covered angular ranges of 90–176 mrad and 11–22 mrad, respectively. Structure modeling and image simulations were carried out using the software package of QSTEM [14].

### 3. Results and discussion

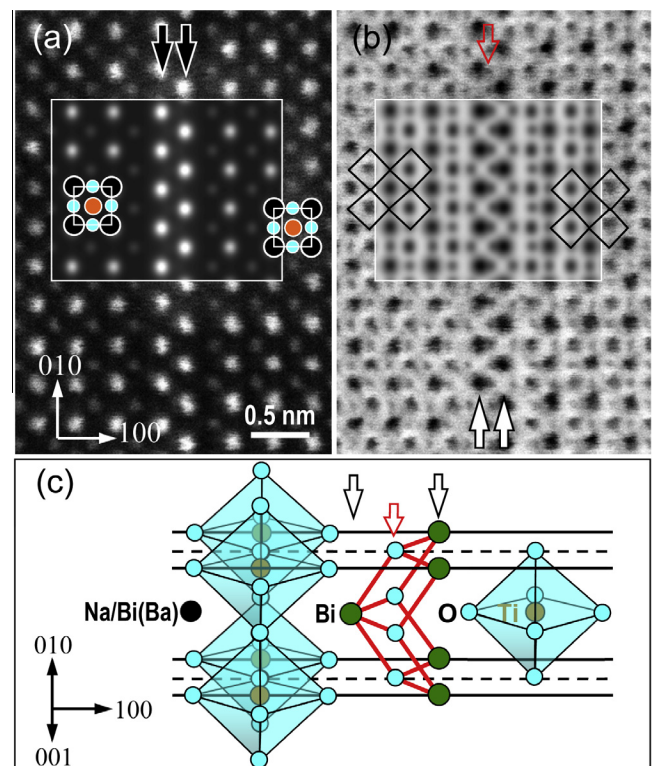
Fig. 1(a) shows a low-magnification bright-field (BF) image of 0.95NBT–0.05BT films on NiO recorded in STEM mode. The contrast between 0.95NBT–0.05BT and NiO is visible and the 0.95NBT–0.05BT/NiO interface is indicated by a double-head arrow. In addition, the contrast variations in the 0.95NBT–0.05BT films are seen resulting from the existence of planar defects, which are indicated by thick open arrows. A high-resolution HAADF image of the 0.95NBT–0.05BT/NiO interface is displayed in Fig. 1(b), which is the part marked by a rectangular in Fig. 1(a). The viewing direction is the [001] zone axis of 0.95NBT–0.05BT (In the following, we neglect the slight rhombohedral distortions of 0.95NBT–0.05BT and adopt the notation for cubic-perovskite in order to facilitate the discussion [9]). Under HAADF imaging conditions, the atom positions show bright contrast (bright dots) under dark background and the intensity of the bright dots is roughly proportional to  $Z^2$  ( $Z$ , atomic number) of the atom columns [11], which allows to determine the chemistry of various columns of the 0.95NBT–0.05BT films. The 0.95NBT–0.05BT/NiO interface looks very sharp and no secondary phases were observed at the interface. NiO has a crystalline structure confirmed by X-ray diffraction [10]. Selected area electron diffraction (SAED) was performed on the heterostructure of 0.95NBT–0.05BT/NiO and there is no evidence of a crystallographic orientation relationship between the

piezoelectric films and NiO. Based on the contrast variation in the 0.95NBT–0.05BT films, the existence of planar defects in the films can be found with the habit plane parallel to the  $\langle 100 \rangle$  plane of 0.95NBT–0.05BT, as indicated by vertical arrows. It is noted that two types of morphology of the planar defects (namely, type I and type II, respectively) exist. Usually, the planar defects start from the interface region and penetrate the whole 0.95NBT–0.05BT grains.

Fig. 2(a) shows an atomic-resolution HAADF image of the 0.95NBT–0.05BT films containing a planar defect of type I, recorded along the [001] zone axis of 0.95NBT–0.05BT. In the perfect area of 0.95NBT–0.05BT, brighter dots are Na/Bi(Ba) atom columns and the less bright ones are Ti columns. The intensity of oxygen columns cannot be detected due to its low nuclear charge value. It can be seen that the continuity of perovskite structure is interrupted by the planar fault. The perovskite structure model of 0.95NBT–0.05BT was superposed on the HAADF image of the perfect area of 0.95NBT–0.05BT film, which demonstrates a relative displacement  $a/2[010]$  ( $a$  is the parameter of perovskite unit cell) between the left and the right part of 0.95NBT–0.05BT in the projected (001) plane. In addition, the image intensity of the atom columns in the two fault planes, denoted by a pair of vertical arrows, is higher than that of the Na/Bi(Ba) columns in the perfect area of the 0.95NBT–0.05BT films. We assume that the atomic columns in the two fault planes consist of Bi atoms. Along [100] direction, the interlayer spacing between Bi and its neighboring Na/Bi(Ba)



**Fig. 1.** (a) A low-magnification STEM bright-field image of the 0.95NBT–0.05BT/NiO heterostructure. (b) A high-resolution HAADF image of the 0.95NBT–0.05BT/NiO interface, taken from the part marked by a rectangular in (a). The 0.95NBT–0.05BT/NiO interface is indicated by two double-head arrows. Planar defects in 0.95NBT–0.05BT film area are indicated by vertical arrows. Two types of planar defects are denoted as type I and type II, respectively.



**Fig. 2.** Atomic-resolution HAADF (a) and ABF image (b) of the 0.95NBT–0.05BT films containing type I planar defects, recorded simultaneously along the [001] zone axis of 0.95NBT–0.05BT. (c) The structure model of the planar defects. Two Bi atomic planes are indicated by a pair of vertical arrows, and O atomic plane by a vertical red arrow. The perovskite structure unit of 0.95NBT–0.05BT is inserted in (a) to show the relative displacement across the planar defect. The oxygen octahedra in 0.95NBT–0.05BT are shown in (b) by the black diamonds. The simulated HAADF and ABF images are inserted in (a) and (b), which were calculated for a specimen thickness of 19.5 nm,  $C_s$  value of 1  $\mu\text{m}$  and a defocus value of 1.9 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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