

© 2017, Elsevier. Licensed under the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International  
<http://creativecommons.org/licenses/by-nc-nd/4.0/>

## Accepted Manuscript

The growth of non-c-axis-oriented ferroelectric BLT thin films on silicon using ZnO buffer layer

David Coathup, Zheng Li, Xiaojing Zhu, Haitao Ye

PII: S0167-577X(17)31012-1  
DOI: <http://dx.doi.org/10.1016/j.matlet.2017.06.112>  
Reference: MLBLUE 22824

To appear in: *Materials Letters*

Received Date: 31 May 2017  
Revised Date: 16 June 2017  
Accepted Date: 26 June 2017

Please cite this article as: D. Coathup, Z. Li, X. Zhu, H. Ye, The growth of non-c-axis-oriented ferroelectric BLT thin films on silicon using ZnO buffer layer, *Materials Letters* (2017), doi: <http://dx.doi.org/10.1016/j.matlet.2017.06.112>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

# The growth of non-c-axis-oriented ferroelectric BLT thin films on silicon using ZnO buffer layer

David Coathup<sup>1</sup>, Zheng Li<sup>2</sup>, Xiaojing Zhu<sup>3</sup>, Haitao Ye<sup>1,\*</sup>

<sup>1</sup>*Department of Electrical, Electronic and Power Engineering, Aston University, Birmingham, B4 7ET*

<sup>2</sup>*Wuhan Institute of Marine Electric Propulsion, Wuhan, China 430070*

<sup>3</sup>*School of Engineering and Technology, University of Hertfordshire, College Lane, Hatfield, AL10 9AB*

\* email: [h.ye@aston.ac.uk](mailto:h.ye@aston.ac.uk)

## Abstract

Lanthanum-doped bismuth titanate (BLT) thin films were grown on buffered Si substrates using a RF magnetron sputtering system. Electrically conducting ZnO layers were used as an effective buffer layer to facilitate the growth of the ferroelectric thin films. X-ray diffraction data shows the Aurivillius phase structure with the highest diffraction peak (117), indicating non-c-axis-oriented microstructure. Random oriented plate-like grains were observed using scanning electron microscopy. The ferroelectric nature of the film was proved by ferroelectric domain switching under an electrical field.

Key words: **Bismuth titanate, ZnO, Ferroelectrics, Thin films, sputtering**

## Introduction

Aurivillius phase bismuth layer-structured ferroelectrics (BLSFs) have the general formula  $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ , where A is a mono-, di-, or trivalent cation, or a combination of them with cuboctahedral coordination. B is a transition-metal cation suited to octahedral coordination, and m is the number of octahedral layers in the perovskite slab, which varies from 1 to 6 [1]. Grains of BLSFs are plate-like with c-axis along the thickness of each grain. Because the majority of ferroelectric thin film devices utilises the polarization perpendicular to the thickness direction of each grain, it is necessary to prepare BLSFs film with non-c-axis orientation for ferroelectric applications due to the higher polarisation of the a and b-axis compared to the c-axis. However, it is a challenge to prepare films with a non-c-axis direction, because the BLSFs intrinsically possess c-axis-oriented films due to their highly anisotropic structure [2].

Lanthanum-doped bismuth titanate (BLT) is a three layer (m=3) Aurivillius phase compound. BLT is a promising candidate in non-volatile ferroelectric random access memories (FeRAMs) due to its fatigue resistance characteristics[3-4]. For practical applications such as memory devices, BLT materials in the format of thin films are urgently needed for its better congeniality with integrated circuit technology. Experimental methods such as sputtering or pulsed laser deposition are commonly utilized for BLT thin films integration onto silicon [5]. However, the endeavor to integrate BLT directly on Si substrates is challenging due to the substantial lattice mismatch between BLT and Si. Furthermore, the reaction of Si with the ferroelectric materials oxygen components can result in the formation of  $\text{SiO}_2$  or amorphous phases between the layers [6]. This oxide layer may be undesirable in applications because as it forms in series with the Aurivillius film, limiting the applied electric field across the device. The amorphous layer may also be troublesome as it will prohibit the thin film growth. In order to overcome the above challenges and to improve the thin film crystal quality, a thin ZnO film is proposed in this paper as an interface layer between the BLT and the Si substrates before deposition. ZnO is an excellent semiconductor which can be used as a buffer layer for the BLT thin film integration due to its wide bandgap, nontoxicity, affordability and abundance, whilst possessing chemical and thermal stability under plasma processes[7]. It offers the potential to block the elemental diffusion across the BLT films and substrates. These features make it suitable for integration of BLT/ZnO/Si MOS devices. The

lattice parameters of wurzite ZnO are  $a_{\text{zno}} = b_{\text{zno}} = 3.35 \text{ \AA}$  and  $c_{\text{zno}} = 5.2 \text{ \AA}$  and those of tetragonal BLT are  $a_{\text{blt}} = 0.545 \text{ \AA}$ ,  $b_{\text{blt}} = 0.541 \text{ \AA}$  and  $c_{\text{blt}} = 3.282 \text{ \AA}$ . This indicates a lattice mismatch exists between the two, which could lead to the formation of non-c-axis BLT thin films. This paper reports on the growth of non-c-axis-oriented ferroelectric BLT thin films on silicon using ZnO buffer layer, which tends to favor a polar axis lying in-plane rather than out-of-plane.

### Experimental.

A BLT target with Aurivillius phase structure was purchased from Nanoforce Technology Ltd. The crystal structure of BLT was characterised by XRD prior to deposition. For the ZnO thin films deposition, a ZnO target (Advent Research Materials Limited) was utilized. A radio frequency magnetron sputtering apparatus was employed to deposit the BLT and ZnO thin films. P-type silicon (100) wafers were used as substrates throughout the experiments. Silicon substrates were cleaned by sonication in acetone and isopropanol, and then rinsed in de-ionized water, followed by blow drying with  $\text{N}_2$  gas before being loaded into the sputtering chamber. All sputtering deposition was performed with a base pressure of less than  $10^{-4}$  Pa. The BLT films were deposited with an RF power of 150 W and a pure argon atmosphere of 1 Pa, obtained with a gas flow rate of 14 sccm. ZnO thin films were deposited with an RF power of 300W, whilst the other conditions remained the same as for BLT films. The target-substrate distance was 15 cm and all depositions were carried out at ambient temperatures without external heating. The thickness of films was controlled by varying the deposition time. To analyse the effect of the ZnO interface layer on the crystallinity of BLT, 170nm thick ZnO interface films were deposited onto Si substrates firstly. A BLT layer with 300 nm thickness was then deposited. The BLT films were annealed at  $550^\circ\text{C}$ ,  $650^\circ\text{C}$ ,  $700^\circ\text{C}$  and  $750^\circ\text{C}$  for 60 minutes in ambient atmosphere for comparison studies. In order to evaluate the ferroelectric properties, optimised BLT thin films (annealed at  $700^\circ\text{C}$ ) were chosen, which possesses the minimal pyrochlore phase with the strong BLT peak presence. These films were utilised in a vertical WC/BLT/ZnO/Si/WC structure. WC is used as the electronic contacts as it has a high temperature tolerance. The crystal structures of the BLT thin films were characterized by X-ray diffraction (XRD), using an X'PERT-PRO with a wavelength of  $1.54 \text{ \AA}$ . The surface morphology was observed by scanning electron microscope (SEM). The current–electric field (I-E) and electrical displacement–electric field (D–E) hysteresis loops were measured using a ferroelectric hysteresis measurement tester at Nanoforce Technology Ltd.

## Results and Discussion

Fig.1 presents XRD pattern of the ZnO films on Si and the BLT thin films with different annealing conditions deposited on interface layers. The diffraction pattern of the ZnO interface layer (Fig.1.A) presents a single broad peak located at  $33.7^\circ$ , which is characteristic of (100) orientated ZnO [8]. The wide shoulder above  $35^\circ$  indicates the presence of secondary orientation of ZnO with weak crystallinity. Fig.1.B presents the plot of the as-deposited BLT thin film on the ZnO interface layer. No characteristic peaks of Aurivillius phase BLT are present, indicating the film is amorphous. Fig.1.C-F present the diffraction patterns of BLT thin films on as-deposited ZnO interface layers after annealing at  $550^\circ\text{C}$ ,  $650^\circ\text{C}$ ,  $700^\circ\text{C}$  and  $750^\circ\text{C}$ , respectively. After annealing, the films present Aurivillius phases, with a dominant non-c-axis-oriented (117) crystal plane, which indicate that the films are non-c-axis oriented because all the highest peaks of three layerd BLSF is  $(1\ 1\ 2m+1)$  [9]. Additionally, a peak corresponding to (002) ZnO is present for annealed BLT thin films, indicating the ZnO layer has undergone a change in crystallinity after annealing. A Bi-deficient Pyrochlore ( $\text{Bi}_2\text{Ti}_2\text{O}_7$ ) secondary phase, labeled 'P' is also observed in the XRD of films annealed at temperatures of  $700^\circ\text{C}$  and  $750^\circ\text{C}$ , which can be attributed to bismuth oxide loss at high temperatures due to their volatility [10].

To further investigate the effect of a ZnO interface layer on surface morphology, the films were studied by scanning electron microscopy. Fig.2 presents the surface morphology of BLT thin films on as-deposited ZnO interface layers and the surface morphology of the ZnO interface layer. Fig.2.A presents the morphology of the ZnO interface layer, indicating an amorphous phase. Fig.2.B presents the as-deposited BLT film on ZnO interface layers, which shows a non-crystalline amorphous structure. Fig.2.(C-F) demonstrate BLT thin films annealed at  $550^\circ\text{C}$ ,  $650^\circ\text{C}$ ,  $700^\circ\text{C}$  and  $750^\circ\text{C}$ , respectively.

The grain morphology changed from almost equi-axed for C and D to platelet for E and F. Nanoparticles produced by RF Sputtering have equi-axed shapes and form agglomerates. The shape of the nanoparticles and their agglomerates are still preserved in the bulk ceramic sample annealed up to  $650^\circ\text{C}$ . With increasing annealing temperature, limited grain growth

takes place at 700°C accompanied by a vanishing of the initial agglomerates to form large equi-axed grains. At 750°C, anisotropic grain growth has occurred, which results in micron-size, faceted platelet grains. After annealing, it is clear that all the BLT films have randomly orientated plate-like grains [11], which is consistent with the XRD data in Fig.1.

Fig.3 shows the current-electric field (I-E) and electrical displacement-electric field (D-E) loops of optimised BLT thin films on silicon substrates with as-deposited ZnO interface layers, measured at 20 Hz. The current peak near 35kV/cm in the I-E loop can be attributed to the ferroelectric domain switching along a-b-direction in BLT platelet-like grains, which indicates the ferroelectric nature of the film [12]. The D-E loop in Fig.3 (b) presents a ferroelectric hysteresis curve with a remanent polarisation of  $2P_r=6.72 \mu\text{C}/\text{cm}^2$  and coercive field  $2E_c$  of 120kV/cm under the applied electric field of 180kV/cm. Zhai et.al. reported the growth of preferred c-axis-oriented ferroelectric BLT thin films using  $\text{LaNiO}_3$  buffer layer. Their ferroelectric hysteresis curve is saturated (with a remanent polarisation  $2P_r$  of  $3.6 \mu\text{C}/\text{cm}^2$  and coercive field  $2E_c$  of 90kV/cm) at the same applied electric field value of 180kV/cm [13]. In comparison, the remanent polarisation value for BLT films with non-c-axis orientation is larger than their reported value for preferred c-axis-oriented BLT films. This improvement can be attributed to the larger and platelet-like grains of the non-c-axis-orientated BLT films. The domain walls in larger and platelet-like grain are easier to be switched under external field, whilst smaller domains in peg-like shape grains seem more stable. It is worth noting that ZnO as buffer layers may induce additional coupling between BLT and ZnO due to the possible junction formation at the interface between the ZnO and BLT layers, which will induce space charge region to influence the overall ferroelectric properties [14].

## Conclusion

In summary, the non-c-axis-oriented BLT thin films were successfully grown on buffered ZnO/Si substrates by RF magnetron sputtering system. The dominated (117) diffraction peak in X-ray diffraction pattern reveals the non-c-axis-oriented structure. With the increase of the annealing temperature, the grain structure were turn to be more anisotropic. Ferroelectric domain switching within *a-b* plane observed in I-V loops confirmed the ferroelectric nature

of the BLT film. The remanent polarisation (2Pr) of the BLT film annealed at 700°C was 6.72  $\mu\text{C}/\text{cm}^2$ .

### Acknowledgement

This work was supported by EU H2020 Project (No 734578).

### Reference

- 1 A. Z. Simoes, A. H. M. Gonzalez, C. S. Riccardi, E. C. Souza, F. Moura, M. A. Zaghete, E. Longo, and J. A. Varela, *J. Electroceram.* **13** (1), 65 (2004).
- 2 H. N. Lee, D. Hesse, N. Zakharov, and U. Gosele, *Science* **296** (5575), 2006 (2002).
- 3 B. H. Park, B. S. Kang, S. D. Bu, T. W. Noh, J. Lee, and W. Jo, *Nature* **401** (6754), 682 (1999).
- 4 Y. Ding, J. S. Liu, H. X. Qin, J. S. Zhu, and Y. N. Wang, *Appl. Phys. Lett.* **78** (26), 4175 (2001).
- 5 M. P. Besland, H. D. A. Aissa, P. R. J. Barroy, S. Lafane, P. Y. Tessier, B. Angleraud, M. Richard-Plouet, L. Brohan, and M. A. Djouadi, *Thin Solid Films* **495** (1-2), 86 (2006).
- 6 E. Rokuta, Y. Hotta, T. Kubota, H. Tabata, H. Kobayashi, and T. Kawai, *Appl. Phys. Lett.* **79** (3), 403 (2001).
- 7 B. Singh, Z. A. Khan, I. Khan, and S. Ghosha, *Appl. Phys. Lett.* **97** (24) (2010).
- 8 A. K. Zak, R. Razali, W. H. A. Majid, and M. Darroudi, *Int J Nanomed* **6**, 1399 (2011).
- 9 H. X. Yan, H. T. Zhang, M. J. Reece, and X. L. Dong, *Appl. Phys. Lett.* **87** (8) (2005).
- 10 J. E. Alfonso, J. J. Olaya, C. M. Bedoya-Hincapie, J. Toudert, and R. Serna, *Materials* **7** (5), 3427 (2014).
- 11 H. T. Zhang, H. X. Yan, H. P. Ning, M. J. Reece, M. Eriksson, Z. J. Shen, Y. M. Kan, and P. L. Wang, *Nanotechnology* **20** (38) (2009).
- 12 H. X. Yan, F. Inam, G. Viola, H. Ning, H. Zhang, Q. Jiang, T. Zeng, Z. Gao, and M. Reece, *J. Journal of Advanced Dielectrics* **1** (1), 107 (2011).
- 13 J. Zhai, H. Chen, *Applied Physics Letters* **442** (3), 82 (2003).
- 14 N. Ashkenov, M. Schubert, E. Twerdowski, H. v. Wenckstern, B.N. Mbenkum, H. Hochmuth, M. Lorenz, W. Grill, M. Grundmann, *Thin Solid Films* **486**, 153 (2005).

## Figure Caption

Fig.1. XRD patterns of (A) ZnO interface layer on Si(100); (B) BLT thin film on ZnO/Si substrate without annealing; (C) BLT thin film on ZnO/Si substrate annealed at 550°C, (D) BLT thin film on ZnO/Si substrate annealed at 650°C, (E) BLT thin film on ZnO/Si substrate annealed at 700°C, (F) BLT thin film on ZnO/Si substrate annealed at 750°C. Pyrochlore phase peak labelled 'P'.

Fig.2. SEM images of surface morphology of (A) as-deposited ZnO; (B) As-deposited BLT on ZnO/Si, (C) 550°C annealed BLT; (D) 650°C annealed BLT; (E) 700°C annealed BLT; (F) 750°C annealed BLT .

Fig.3. *I-E*, *D-E* hysteresis loops of BLT thin films annealed at 700°C at 180kV/cm and 20Hz.

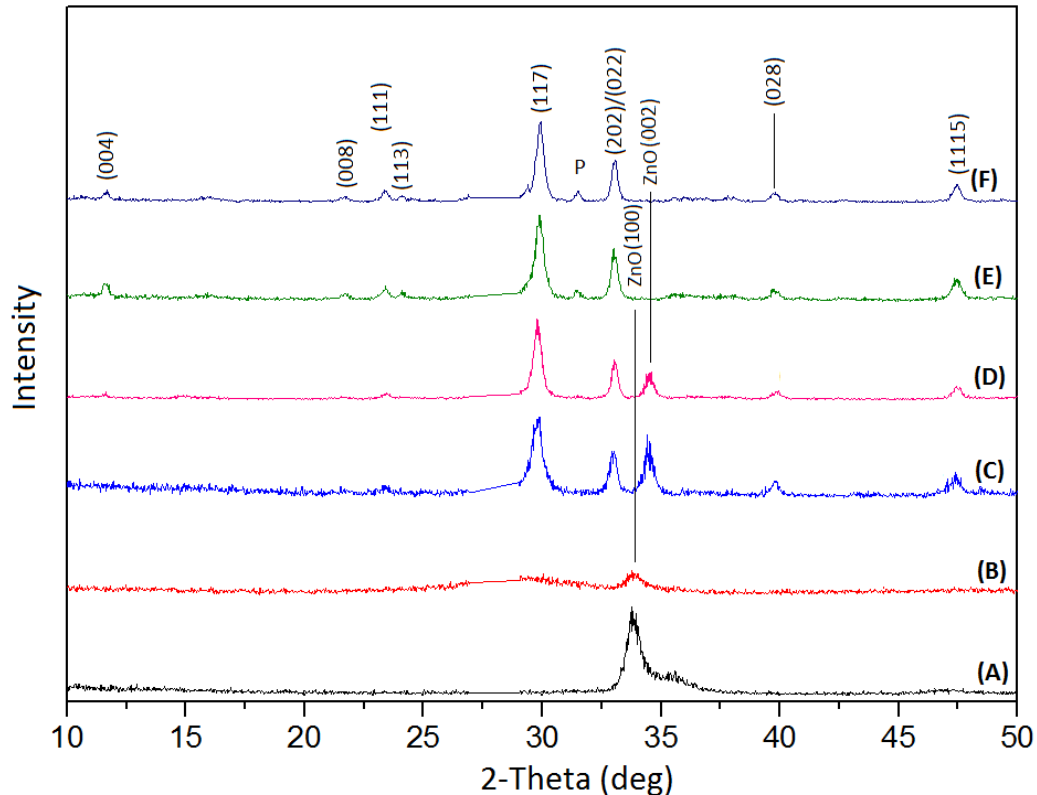


Figure 1



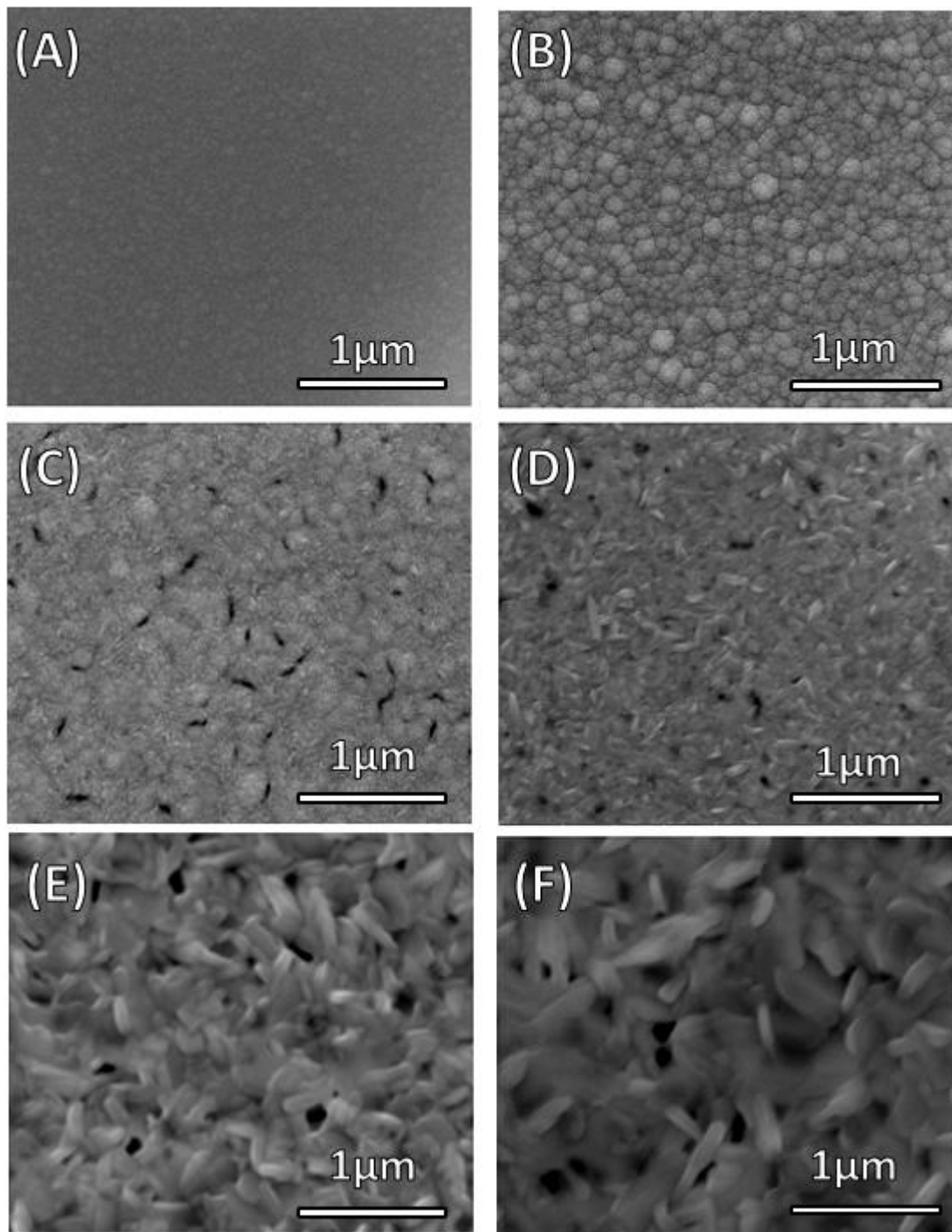


Figure 2

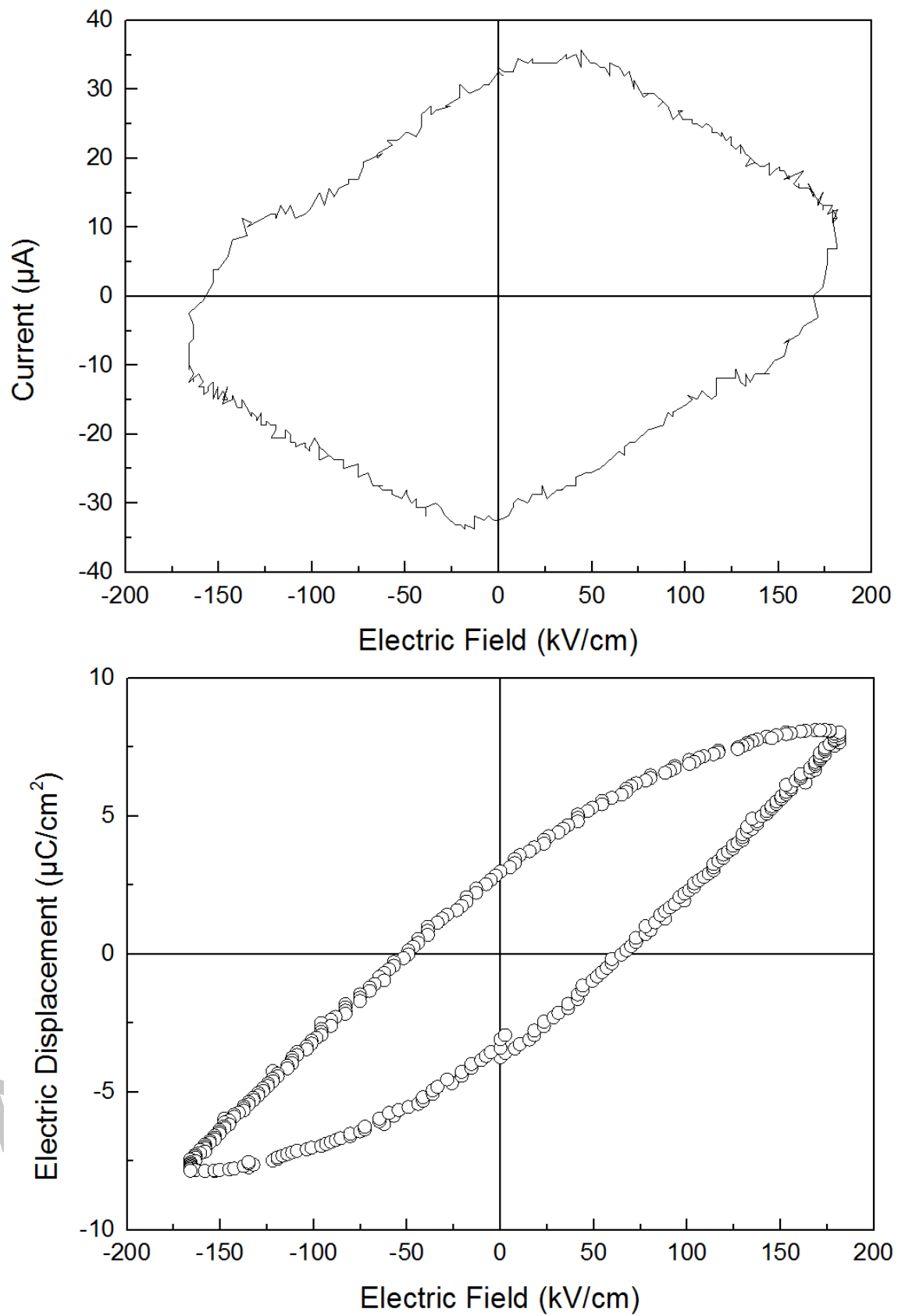


Figure 3

### Highlights

La-doped bismuth titanate (BLT) thin films were grown on Si substrates using ZnO buffer Layers.

ZnO buffer layer facilitates the formation of non-c-axis-oriented microstructure.

BLT films with non-c-axis-oriented grains shows stronger ferroelectric domain switching.

ACCEPTED MANUSCRIPT