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Fabrication of 109° periodic domain walls with bottom electrode in BiFeO3 thin films

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Abstract:	A variety of exiting phenomenon have been discovered at 109° domain walls in BiFeO3 thin films, such as domain wall conductivity, photovoltaic effects, and magnetoelectric coupling effects. Controlling those physical properties by an electric field plays a key role in realizing the nanoelectric devices. Therefore, it is critical to fabricate 109° periodic domain walls with bottom electrode. However, the introduction of bottom electrode favors the formation of 71° domain structure due to the electrostatic boundary conditions. In this study, pulsed laser deposition is used to produce multilayer epitaxial thin films. A 25% La doping BiFeO3 layer is inserted as the dielectric spacer between bottom electrode SrRuO3 layer and pure BiFeO3, enabling the fabrication of 109° periodic domain walls engineered by an interface effect-depolarization field. Moreover, the fabrication of 109° domain structure with bottom electrode enables the study of its switching behavior. This protocol provides a novel route to produce 109° periodic domain walls and opens a new pathway to explore fascinating phenomena such as room temperature electric field control of exchange bias in ferromagnet/BiFeO3 system and room temperature multiferroic vortices in BiFeO3.
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TITLE:
Fabrication of 109° Periodic Domain Walls with a Bottom Electrode in $BiFeO_3$ Thin Films

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SHORT ABSTRACT:
109° periodic domain walls can successfully be fabricated by introducing a dielectric La-$BiFeO_3$ layer between a bottom electrode and a ferroelectric $BiFeO_3$ layer, enabling the study of the switching behavior of a 109° domain structure and the investigation of the electric field control of exchange bias in a ferromagnet/$BiFeO_3$ system.

LONG ABSTRACT:
A variety of exciting phenomena have been discovered using 109° domain walls in $BiFeO_3$ thin films, such as domain wall conductivity, photovoltaic effects, and magnetoelectric coupling effects. The control of these physical properties with an electric field plays a key role in the development of nanoelectric devices. Therefore, it is critical to fabricate 109° periodic domain walls with a bottom electrode. However, the introduction of a bottom electrode favors the formation of a 71° domain structure due to the electrostatic boundary conditions. In this study, pulsed laser deposition (PLD) is used to produce multilayer epitaxial thin films. A 25% La doping $BiFeO_3$ layer is inserted as the dielectric spacer between the bottom electrode $SrRuO_3$ layer and the pure $BiFeO_3$ layer, enabling the fabrication of 109° periodic domain walls engineered by an

interface effect-depolarization field. Moreover, the fabrication of the 109° domain structure with a bottom electrode enables the study of its switching behavior. This protocol provides a novel route to produce 109° periodic domain walls and opens a new pathway to explore fascinating phenomena, such as the room-temperature electric field control of exchange bias in a ferromagnet/$BiFeO_3$ system and room-temperature multiferroic vortices in $BiFeO_3$.

INTRODUCTION:

Domain wall functionalities in $BiFeO_3$ thin films, such as domain wall conductivity[1], photovoltaic effects[2], magnetism[3], and magnetoelectric coupling[4], have inspired many studies on the fabrication and manipulation of the domain structures[5-7]. Periodically ordered 71°, 109°, and 180° stripe domains have been obtained by tuning the film thickness effects, misfit strain effects, and electrostatic boundary conditions[8-11]. The periodic 71° stripe domain structure can be produced on thick $SrRuO_3$ bottom electrodes and can be reversibly controlled under an electric field[8], which has promoted a series of seminal works on the electric-field control of magnetism in the ferromagnet/multiferroic $BiFeO_3$ system[4, 12-15.] However, the pure 109° stripe domain structure can only exist without a (or with an ultra-thin) $SrRuO_3$ bottom electrode[8], making it typically unstable or unresponsive under an applied electric field and inhibiting the study of the switching behavior of 109° domains. Moreover, a large exchange bias has been demonstrated in the ferromagnet/$BiFeO_3$ system with the 109° $BiFeO_3$ domain walls[16,17]. Thus, the successful fabrication of a 109° domain structure with a bottom electrode is promising for controlling exchange bias using an electric field. This has great potential application to low-energy-consumption, non-volatile magnetoelectronic memory devices.

Our previous study[18] revealed a novel approach to precisely control the domain structure in $BiFeO_3$ thin films by tuning the depolarization field with a dielectric layer. In the $BiFeO_3/SrRuO_3/DyScO_3$ stack without La-$BiFeO_3$, the screening effects at the ferroelectric ($BiFeO_3$)/metallic ($SrRuO_3$) interface enable the formation of 71° domains, while the introduction of the La-$BiFeO_3$ dielectric space layer enables an increase in the distance between the screening charges from the $SrRuO_3$ and $BiFeO_3$. This leads to a reduction of the screening effects and thus an increase in the depolarization field. Consequently, the 71° stripe domain is destabilized and a 109° stripe domain structure forms to decrease the energy cost due to the strong depolarization field.

In this work, we focus on the fabrication of 109° periodic domain walls with a bottom electrode in $BiFeO_3$ thin films by introducing a La-$BiFeO_3$ dielectric layer. The detailed protocol describes how to grow the multilayer thin films using PLD and how to use piezoresponse force microscopy (PFM) to measure the 109° domain structure and study its switching behavior. The typical PLD system is shown in **Figure 1**. This protocol can help to increase the reproducibility of the fabrication of 109° periodic domain walls and promote the study of domain wall functionality.

PROTOCOL:

1. Substrate Preparation

1.1. Clean a 5 mm × 5 mm × 0.5 mm single-crystal $DyScO_3$ (110) substrate with acetone in an ultrasonic cleaner for 5 min.

1.2. Rinse the substrate with acetone for 5 s and transfer it to isopropyl alcohol. Clean it for 5 min in the ultrasonic cleaner.

1.3. Rinse the substrate with isopropyl alcohol for 5 s and dry it using N_2 flow.

1.4. Mount the substrate on a heater with silver paint and then put the heater on a hot plate to dry the silver paint for 10 min at 100 °C.

1.5. After the heater cools down to room temperature, blow it with N_2 flow. Mount it into the PLD chamber.

Note: The protocol can be paused here.

2. PLD Setup

2.1 Mount a $SrRuO_3$ target, a $BiFeO_3$ target, and a 25% La doping $BiFeO_3$ (La-$BiFeO_3$) target in the PLD chamber.

2.2 Set the target-to-substrate distance to 50 mm.

2.3 Align the laser light path to focus the laser spot on the target. Attach a piece of sensitive paper on the target and move the focusing lens to a proper position to obtain uniform laser spots, which will ensure the homogeneity of the laser energy.

Note: The target will rotate with roto-translational motion to avoid overheating the target during film growth.

2.4 Measure the laser energy outside and inside the laser window using a power meter to calculate the energy loss rate.

Note: The loss rate increases with increasing growth time due to the coating on the laser window during deposition. Here, the laser window is cleaned every other day.

2.5 Pump the chamber with a mechanical pump until the vacuum is less than 10 Pa. Use the turbo pump to obtain a high vacuum ($< 5 \times 10^{-4}$ Pa).

Note: The protocol can be paused here.

3 **Selection of Deposition Parameters**

3.1 Adjust the pumping speed by tuning the gate valve. Inflate oxygen into the chamber to create oxygen pressure of 13 Pa.

3.2 Heat up the heater to 700 °C at a rate of 20 °C/min and anneal the substrate for 10 min.

3.3 Start the pulsed laser and set the desired laser energy for $SrRuO_3$ growth by changing the voltage. Measure the laser energy using a power meter at a laser frequency of 2 Hz.

4 **Growth of Multilayer Films**

4.1 Clean the $SrRuO_3$ target surface at a frequency of 10 Hz for 3 min.

4.2 Grow $SrRuO_3$ epitaxial thin film on a (110)-oriented $DyScO_3$ substrate at 10 Hz for 6 min using PLD.

Note: The growth temperature should be 700 °C and the oxygen partial pressure should be 13 Pa.

4.3 Tune the heater temperature to 690 °C and clean the La-$BiFeO_3$ target surface at a frequency of 10 Hz for 3 min.

4.4 Start the growth of the La-$BiFeO_3$ layer for 10 min at 10 Hz.

Note: The growth temperature should be 690 °C and the oxygen partial pressure should be 13 Pa.

4.5 Clean the $BiFeO_3$ target surface at a frequency of 10 Hz for 3 min.

4.6 Adjust the frequency of the pulsed laser to 5 Hz and start to grow the $BiFeO_3$ layer for 40 min at 690 °C under oxygen partial pressure of 13 Pa.

4.7 Close the gate valve and inflate oxygen to into the chamber. Cool down the sample at 10 °C/min in a 10,000-Pa oxygen atmosphere.

4.8 Open the chamber after the heater temperature is below 80 °C and remove the sample from the heater.

5 **PFM Measurement**

5.1 Attach the sample to a thin metal plate and contact the bottom electrode with the plate using silver paint.

5.2 Take the PFM measurement of the sample with the cantilever along (110) under the PFM mode to capture 109° domain structure images.

Note: The PFM scanning size should be 5 µm × 5 µm.

5.3 Apply -6 V in a 3 µm × 3 µm box to study the switching behavior of the 109° domain structure.

5.4 Capture the 5 µm × 5 µm PFM images after -6-V switching.

REPRESENTATIVE RESULTS:

The multilayer $BiFeO_3$/La-$BiFeO_3$/$SrRuO_3$ films on the $DyScO_3$ (110) substrate are produced by PLD, and the heterostructure stack is shown in **Figure 2**. To obtain the 109° domain structure with a bottom electrode, a thin dielectric layer of La-$BiFeO_3$ is inserted between the $SrRuO_3$ bottom electrode and the ferroelectric $BiFeO_3$ layer.

As demonstrated in our previous work[18], the thickness of the La-$BiFeO_3$ layer is crucial to the formation of pure 109° domain walls. An ultra-thin La-$BiFeO_3$ layer (< 10 nm) would lead to mixed 71° and 109° domain walls. In this protocol, thicker La-$BiFeO_3$ film layers (>10 nm) are grown to achieve a pure 109° domain structure.

By carefully controlling the PLD growth parameters, including the laser path alignment, laser energy, oxygen pressure, and heater temperature, 109° domain walls can be fabricated in the $BiFeO_3$/La-$BiFeO_3$/$SrRuO_3$/$DyScO_3$ sample, as shown in the PFM data (**Figure 3**). The switching behavior of the 109° domain structure has also been studied by applying a -6-V voltage to the sample, as displayed in **Figure 4**. It is revealed that the 109° domain structure with a bottom electrode can be switched to a 71° domain structure.

FIGURE LEGENDS:

Figure 1. Schematic of the PLD system.

Figure 2. Schematic of the heterostructure $BiFeO_3$/La-$BiFeO_3$/$SrRuO_3$/$DyScO_3$ stack.

Figure 3. Topography and out-of-plane and in-plane PFM images of the obtained sample with a 109° domain structure.
The size of the images is 5 µm × 5 µm. Scale bar: 1 µm.

Figure 4. Switching behavior of a 109° domain structure.
Topography and out-of-plane and in-plane PFM images after a -6-V voltage switch. The size of the images is 5 µm × 5 µm, and the size of the switched regions within the dashed squares is 3 µm × 3 µm. Scale bar: 1 µm.

DISCUSSION:

PLD is a powerful technique to fabricate complex oxide epitaxial thin films[19]. Using this technique, many investigations have been carried out on $BiFeO_3$ thin films[13, 20-22]. As one of the most striking aspects, domain walls are widely studied due to a wealth of fascinating phenomena[1-3], such as domain wall conductivity and enhanced magnetism at a 109° domain wall. However, a 109° domain structure can only exist without a (or with an ultra-thin) bottom electrode[8], inhibiting the study of electric field control of the related physical phenomena. In this study, 109° periodic domain walls with a bottom electrode are produced in $BiFeO_3$ thin films by PLD, which indicates the significance with respect to existing methods[8].

The PLD growth conditions (including laser energy, growth temperature, and oxygen pressure) of high-quality $BiFeO_3$, La-$BiFeO_3$, and $SrRuO_3$ thin films are critical to this protocol. In addition, the selection of the La doping content plays a key role in obtaining the 109° domain structure. Our unpublished data show that La-$BiFeO_3$ is still ferroelectric when the La doping content is less than 18%, which would not lead to the formation of 109° periodic domain walls in the $BiFeO_3$/La-$BiFeO_3$/$SrRuO_3$/$DyScO_3$ stack. Non-ferroelectric 25% La-$BiFeO_3$ is used as a dielectric layer in this study.

One of the limitations of this technique is that the maximum size of the sample can only be 1 cm × 1 cm; otherwise, the film would not be uniform. The substrate selection of $DyScO_3$—which offers anisotropic strain, excluding two of the possible structural variants, to yield a 109° stripe domain structure—is another possible limitation, while other substrates, including $SrTiO_3$, $LaAlO_3$, *etc.* cannot provide the required anisotropic strain.

Previous studies[23] demonstrated that, due to the interplay between strain, depolarization field, and gradient energies, topological ferroelectric vortices can be produced in $PbTiO_3$/$SrTiO_3$ superlattices. The method shown in this protocol provides a possible application to explore the room-temperature multiferroic vortices in the $BiFeO_3$ system. Furthermore, it can be used to control the ferroelectric polarization or domain structures in ferroelectric materials, such as $BaTiO_3$ and $PbZr_xTi_{1-x}O_3$.

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DISCLOSURES:
The authors declare no conflicts of interest.

REFERENCES:
1. Seidel, J. *et al*. Conduction at domain walls in oxide multiferroics. *Nat Mater.* **8**, 229-234 (2009).
2. Choi, T., Lee, S., Choi, Y., Kiryukhin, V., Cheong, S.-W. Switchable ferroelectric diode and photovoltaic effect in $BiFeO_3$. *Science* **324**, 63-66 (2009).
3. Lubk, A., Gemming, S., Spaldin, N. A. First-principles study of ferroelectric domain walls in multiferroic bismuth ferrite. *Phys Rev B* **80**, 104110 (2009).
4. Chu, Y. H. *et al*. Electric-field control of local ferromagnetism using a magnetoelectric multiferroic. *Nat Mater.* **7**, 478-482 (2008).

5. Catalan, G., Seidel, J., Ramesh, R., Scott, J. F. Domain wall nanoelectronics. *Rev Mod Phys*. **84**, 119-156 (2012).
6. Giencke, J. E., Folkman, C. M., Baek, S.-H., Eom, C.-B. Tailoring the domain structure of epitaxial $BiFeO_3$ thin films. *Curr Opin Solid St M.* **18**, 39-45 (2014).
7. Chen, D., Gao, X., Liu, J.-M. Domain structures and magnetoelectric effects in multiferroic nanostructures. *MRS Commun.* **6**, 330-340 (2016).
8. Chu, Y. H. *et al*. Nanoscale Control of Domain Architectures in $BiFeO_3$ Thin Films. *Nano Lett.* **9**, 1726-1730 (2009).
9. Chen, Z. *et al*. 180° Ferroelectric Stripe Nanodomains in $BiFeO_3$ Thin Films. *Nano Lett.* **15**, 6506-6513 (2015).
10. Streiffer, S. K. *et al.* Domain patterns in epitaxial rhombohedral ferroelectric films. I. Geometry and experiments. *J Appl Phys.* **83**, 2742-2753 (1998).
11. Huang, C. W. *et al.* Stability and crossover of 71° and 109° domains influenced by the film thickness and depolarization field in rhombohedral ferroelectric thin films. *J Appl Phys.* **110**, 014110 (2011).
12. Zhao, T. *et al*. Electrical control of antiferromagnetic domains in multiferroic $BiFeO_3$ films at room temperature. *Nat Mater.* **5**, 823-829 (2006).
13. Heron, J. T. *et al*. Deterministic switching of ferromagnetism at room temperature using an electric field. *Nature.* **516**, 370-373 (2014).
14. Dong, S., Liu, J.-M., Cheong, S.-W., Ren, Z. Multiferroic materials and magnetoelectric physics: symmetry, entanglement, excitation, and topology. *Adv Phys.* **64**, 519-626 (2015).
15. Lu, C. L., Hu, W. J., Tian, Y. F., Wu, T. Multiferroic oxide thin films and heterostructures. *Appl Phys Rev.* **2**, 021304 (2015).
16. Martin, L. W. *et al*. Nanoscale control of exchange bias with $BiFeO_3$ thin films. *Nano Lett.* **8**, 2050-2055 (2008).
17. Bea, H. *et al*. Mechanisms of exchange bias with multiferroic $BiFeO_3$ epitaxial thin films. *Phys Rev Lett*. **100**, 017204 (2008).
18. Chen, D. *et al*. Interface engineering of domain structures in $BiFeO_3$ thin films. *Nano Lett.* **17**, 486-493 (2017).
19. Willmott, P. R., Huber, J. R. Pulsed laser vaporization and deposition. *Rev Mod Phys.* **72**, 315-328 (2000).
20. Wang, J. *et al*. Epitaxial $BiFeO_3$ multiferroic thin film heterostructures. *Science.* **299**, 1719-1722 (2003).
21. Zeches, R. J. *et al*. A Strain-Driven Morphotropic Phase Boundary in $BiFeO_3$. *Science.* **326**, 977-980 (2009).
22. Huang, C. W., Chen, L. Effects of interfaces on the structure and novel physical properties in epitaxial multiferroic $Bifeo_3$ ultrathin films. *Materials.* **7**, 5403-5426 (2014).
23. Yadav, A. K. *et al*. Observation of polar vortices in oxide superlattices. *Nature.* **530**, 198-201 (2016).

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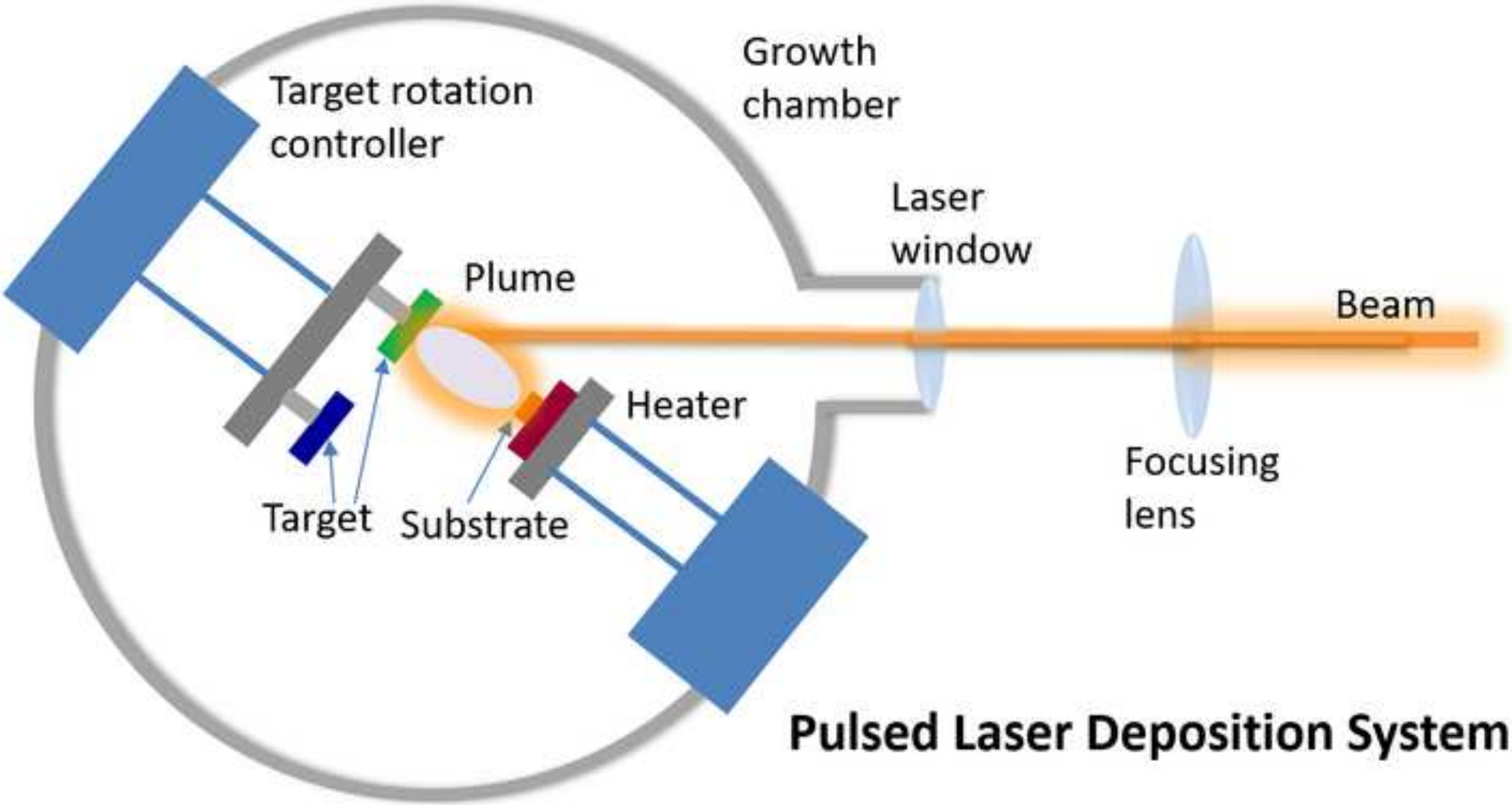

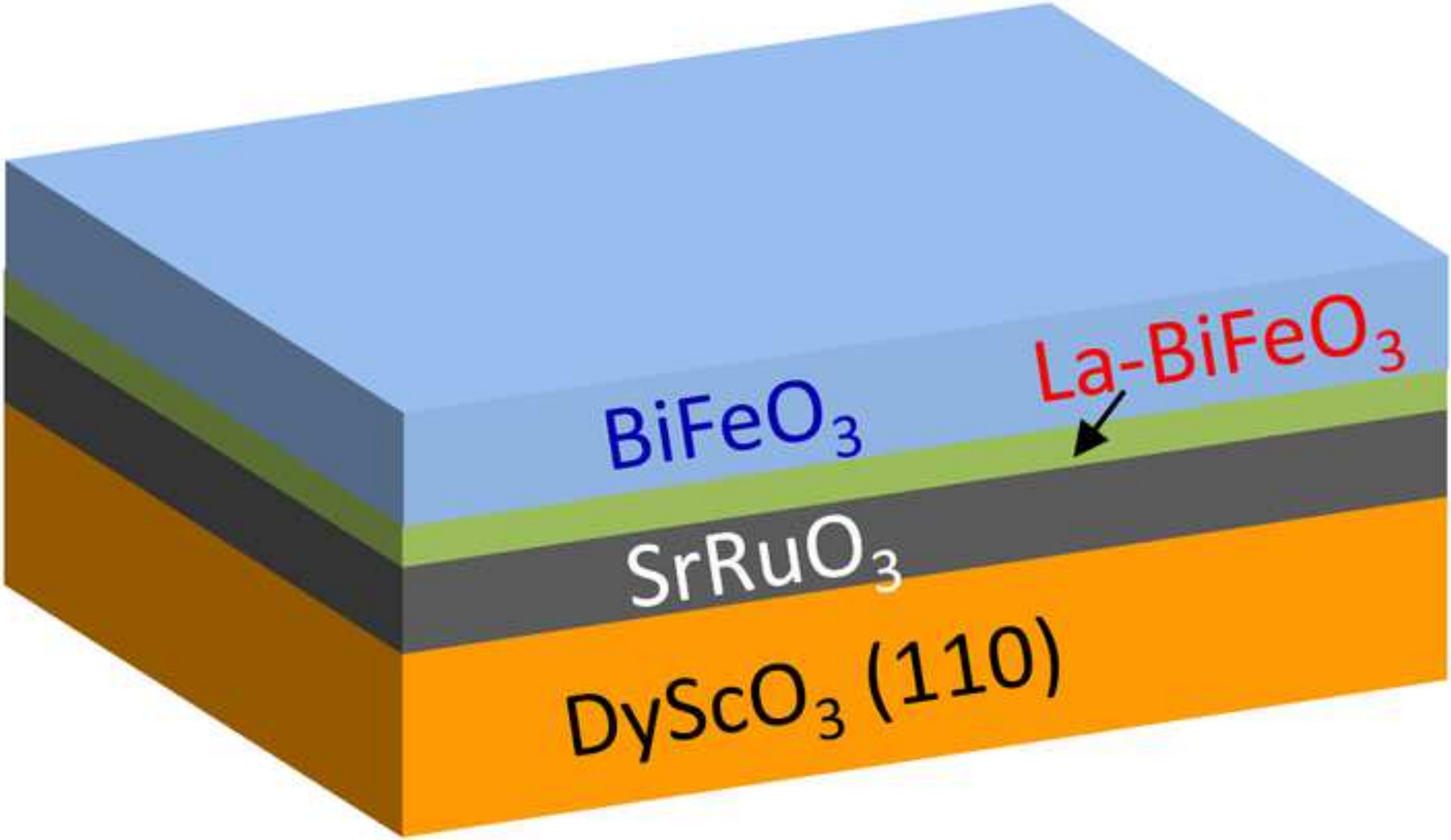
La-BiFeO3
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SrRuO3
DyScO3 (110)

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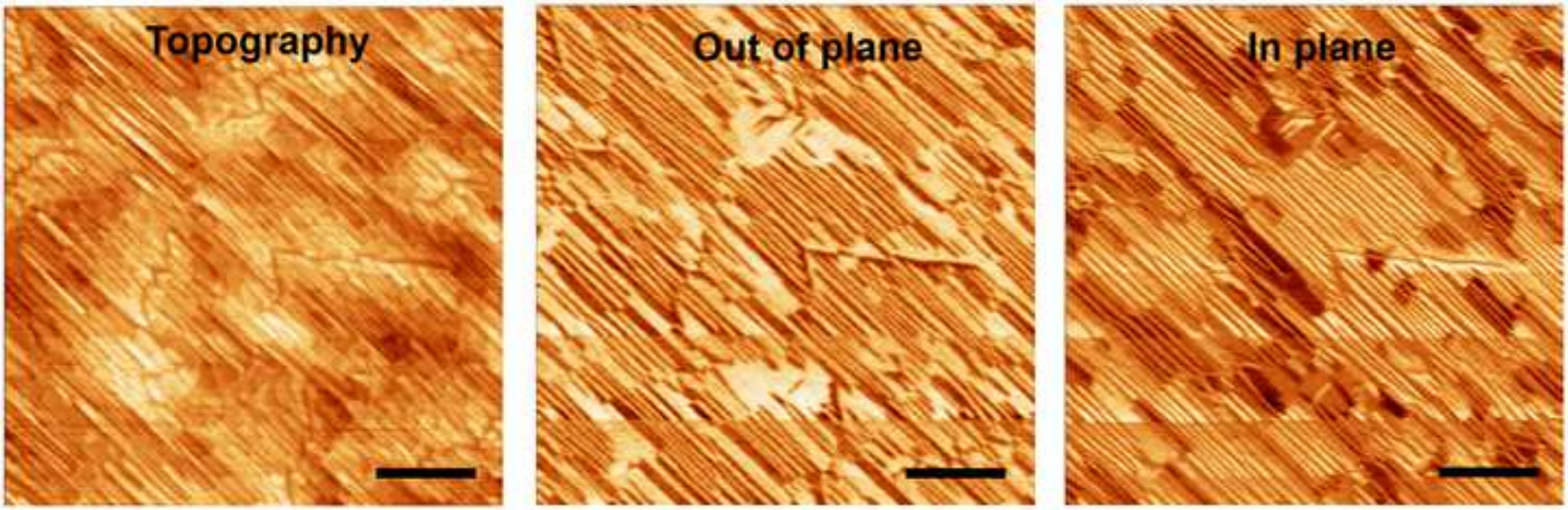

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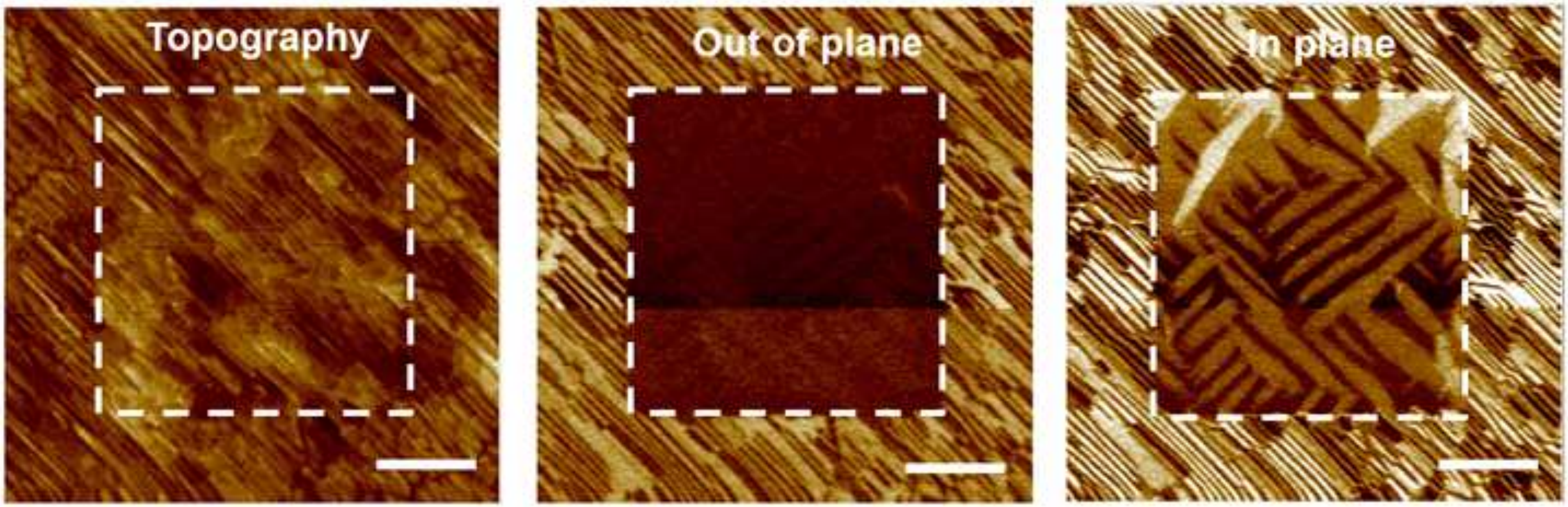

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Dear editor,

Thank you for your comments and the reviewers' suggestions on our manuscript. We have addressed all the comments in the manuscript.

Editorial comments:
Changes to be made by the Author(s):
1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues. The JoVE editor will not copy-edit your manuscript and any errors in the submitted revision may be present in the published version.

Thank you for your suggestions. We have double-checked the spelling and grammar.

2. Please define all abbreviations before use.

Thank you for your suggestions. We have defined all abbreviations before use.

3. Please use focused images of uniform size/resolution (at least 300 dpi).

Thank you for your reminder. We use focused images in the manuscript.

4. Please revise the table of the essential supplies, reagents, and equipment. The table should include the name, company, and catalog number of all relevant materials in separate columns in an xls/xlsx file.

We have updated the table with all the information of relevant materials/equipment.

5. Please include a scale bar for all images taken with a microscope to provide context to the magnification used. Define the scale in the appropriate Figure Legend.

Thank you for your suggestions. We have added a scale bar for the images and defined the scale in the Figure Legend.

6. Please use SI abbreviations for time: h, min, s, etc.

Thank you for your reminder. We use SI abbreviations for time in the manuscript.

7. JoVE cannot publish manuscripts containing commercial language. This includes trademark symbols (™), registered symbols (®), and company names before an instrument or reagent. Please remove all commercial language from your manuscript and use generic terms instead. All commercial products should be sufficiently referenced in the Table of Materials and Reagents.
For example: MFP-3D Infinity Asylum Research, etc.

Thank you for your suggestions. We have removed all commercial language from the manuscript.

8. As we are a methods journal, please revise the Discussion to explicitly cover the following in detail in 3-6 paragraphs with citations:
a) Critical steps within the protocol
b) Any modifications and troubleshooting of the technique
c) Any limitations of the technique
d) The significance with respect to existing methods
e) Any future applications of the technique

Thank you for your suggestions. We have revised the Discussion and covered the details of a)-e) in the manuscript.

Reviewers' comments:
Reviewer #1:
Manuscript Summary:
The manuscript describes experimental details to reliably create the 109 domain walls by introducing a La-BFO spacer.
The 109 domain wall in BFO has attracted a lot of attention due to its functionalities such as domain wall conduction and magnetism as well as the magnetoelectric switching.
As addressed by authors, it has been tantalizing to obtain the stable as-grown state with dense 109 domain walls on a conducting bottom electrode.
Accordingly, this video-based paper will be able to contribute to the advance of multiferroic study based on BFO.
I would like to recommend the manuscript as it is.

Thank you for your positive comments. We hope this work will promote the study of multiferroics and magnetoelectric devices.

Reviewer #2:
Manuscript Summary:
So far, the 109° domain walls attracts more interests than 71° domain walls due to their superior domain wall physical properties. This article reveals a very detailed experimental process for fabricating stabilized 109° BFO thin film, which is hardly obtained while grown on the substrate with SRO bottom electrode. The key point is to insert a dielectric spacer like a 25% La doped BFO thin film to enhance the depolarization field. As a whole, this work provides a general way to stably produce the 109° BFO thin film capable of multiferroic devices.

Thank you for your positive comments of this work.

Minor Concerns:

A minor suggestion in the protocol section, the procedure 4.
To avoid confusing the readers, I suggest to replace the word "pre-deposit" by "Clean the target surface" because during these "pre-deposit" steps, nothing is really deposited on something.

Thank you for your suggestions. We have replaced "pre-deposit" by "clean the target surface" in the manuscript.

Reviewer #3:
Manuscript Summary:
The authors report their findings, namely that fabrication of 109° periodic domain patterns in BFO thin films by inserting a dielectric layer between the bottom electrode and the film. The results demonstrated in this manuscript are interesting and deserves to be published in this well-known journal. However, a minor revision is still needed before being accepted. Additionally, the manuscript is not well written, with examples illustrated below.

Thank you for your positive comments and suggestions.

Minor Concerns:
Comments and questions:
1.Domain patterns are not only determined by depolarization field (as studied in this manuscript), but also remarkably influenced by misfit strain and film thickness in ferroelectric films. Please briefly describe those effects on your system. Additionally, the thickness of BFO film studied in this draft is missing.

Thank you for your suggestions. We have briefly described the misfit strain and thickness effects in the manuscript.

2. The stability and crossover between 71° and 109° domain patterns have been investigated intensively in rhombohedral FE films (JOURNAL OF APPLIED PHYSICS 83, 2742, 1998; JOURNAL OF APPLIED PHYSICS 110, 014110, 2011). Key aspects such as elastic, electrostatic energies and films thickness on the formation of various domains have been analyzed theoretically. However, it is claimed that different rhombohedral domain patterns (from 71° to 109°) can be realized only by controlling the misfit strain in JOURNAL OF APPLIED PHYSICS 83, 2742, 1998. Does the model can be realized experimentally based on your experiences? Meanwhile, how does the domain pattern change if the BFO is deposited on other substrates such as substrates with large compressive or tensile misfit strains, besides DSO?

Thank you for your suggestions. We have briefly described the misfit strain effects in the introduction part. However, we focus on the protocol details to fabricate 109° domain structure in this work as JoVE is a method journal. To avoid the misfit strain effects, we are using the same substrate ($DyScO_3$) in this work. It is worth to mention that not only the domain patterns, but also the phase structures would change if we use

large compressive or tensile misfit strain substrates [Science 326, 977(2009), Phys Rev Lett 109, 247606 (2012)]. Related study is also ongoing in our lab. However, this part is beyond the scope of this research.

3. From the scientific perspective, it is better to cite those original papers listed above (JAP 83, 2742, 1998; JAP 110, 014110, 2011) in the introduction section.

Thank you for your suggestions. We have cited these two papers.

4. Several language and grammar problems(such as a variety of phenomena instead of phenomenon in the abstract part, line 64 metallic instead of metal)

Thank you for your suggestions. We went through the whole manuscript and revised the language and grammar problems.

We hope the revised manuscript is ready for publication. Thank you for your consideration.

Best,
Deyang Chen