**TITLE:**

Fabrication of 109° Periodic Domain Walls with a Bottom Electrode in BiFeO3 Thin Films

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**SHORT ABSTRACT:**

109° periodic domain walls can successfully be fabricated by introducing a dielectric La-BiFeO3 layer between a bottom electrode and a ferroelectric BiFeO3 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/BiFeO3 system.

**LONG ABSTRACT:**

A variety of exciting phenomena have been discovered using 109° domain walls in BiFeO3 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 BiFeO3 layer is inserted as the dielectric spacer between the bottom electrode SrRuO3 layer and the pure BiFeO3 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/BiFeO3 system and room-temperature multiferroic vortices in BiFeO3.

**INTRODUCTION:**

Domain wall functionalities in BiFeO3 thin films, such as domain wall conductivity1, photovoltaic effects2, magnetism3, and magnetoelectric coupling4, have inspired many studies on the fabrication and manipulation of the domain structures5-7. Periodically ordered 71°, 109°, and 180° stripe domains have been obtained by tuning the film thickness effects, misfit strain effects, and electrostatic boundary conditions8-11. The periodic 71° stripe domain structure can be produced on thick SrRuO3 bottom electrodes and can be reversibly controlled under an electric field8, which has promoted a series of seminal works on the electric-field control of magnetism in the ferromagnet/multiferroic BiFeO3 system4, 12-15. However, the pure 109° stripe domain structure can only exist without a (or with an ultra-thin) SrRuO3 bottom electrode8, 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/BiFeO3 system with the 109° BiFeO3 domain walls16,17. 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 study18 revealed a novel approach to precisely control the domain structure in BiFeO3 thin films by tuning the depolarization field with a dielectric layer. In the BiFeO3/SrRuO3/DyScO3 stack without La-BiFeO3, the screening effects at the ferroelectric (BiFeO3)/metallic (SrRuO3) interface enable the formation of 71° domains, while the introduction of the La-BiFeO3 dielectric space layer enables an increase in the distance between the screening charges from the SrRuO3 and BiFeO3. 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 BiFeO3 thin films by introducing a La-BiFeO3 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. Clean a 5 mm × 5 mm × 0.5 mm single-crystal DyScO3 (110) substrate with acetone in an ultrasonic cleaner for 5 min.
   2. Rinse the substrate with acetone for 5 s and transfer it to isopropyl alcohol. Clean it for 5 min in the ultrasonic cleaner.
   3. Rinse the substrate with isopropyl alcohol for 5 s and dry it using N2 flow.

* 1. 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.
  2. After the heater cools down to room temperature, blow it with N2 flow. Mount it into the PLD chamber.

Note: The protocol can be paused here.

1. **PLD Setup**
   1. Mount a SrRuO3 target, a BiFeO3 target, and a 25% La doping BiFeO3 (La-BiFeO3) target in the PLD chamber.
   2. Set the target-to-substrate distance to 50 mm.
   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.

* 1. 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.

* 1. 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 × 10-4Pa).

Note: The protocol can be paused here.

1. **Selection of Deposition Parameters**
   1. Adjust the pumping speed by tuning the gate valve. Inflate oxygen into the chamber to create oxygen pressure of 13 Pa.
   2. Heat up the heater to 700 °C at a rate of 20 °C/min and anneal the substrate for 10 min.
   3. Start the pulsed laser and set the desired laser energy for SrRuO3 growth by changing the voltage. Measure the laser energy using a power meter at a laser frequency of 2 Hz.
2. **Growth of Multilayer Films**
   1. Clean the SrRuO3 target surface at a frequency of 10 Hz for 3 min.
   2. Grow SrRuO3 epitaxial thin film on a (110)-oriented DyScO3 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.

* 1. Tune the heater temperature to 690 °C and clean the La-BiFeO3 target surface at a frequency of 10 Hz for 3 min.
  2. Start the growth of the La-BiFeO3 layer for 10 min at 10 Hz.

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

* 1. Clean the BiFeO3 target surface at a frequency of 10 Hz for 3 min.
  2. Adjust the frequency of the pulsed laser to 5 Hz and start to grow the BiFeO3 layer for 40 min at 690 °C under oxygen partial pressure of 13 Pa.
  3. 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. Open the chamber after the heater temperature is below 80 °C and remove the sample from the heater.

1. **PFM Measurement** 
   1. Attach the sample to a thin metal plate and contact the bottom electrode with the plate using silver paint.
   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.

* 1. Apply -6 V in a 3 µm × 3 µm box to study the switching behavior of the 109° domain structure.
  2. Capture the 5 µm × 5 µm PFM images after -6-V switching.

**REPRESENTATIVE RESULTS:**

The multilayer BiFeO3/La-BiFeO3/SrRuO3 films on the DyScO3 (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-BiFeO3 is inserted between the SrRuO3 bottom electrode and the ferroelectric BiFeO3 layer.

As demonstrated in our previous work18, the thickness of the La-BiFeO3 layeris crucial to the formation of pure 109° domain walls. An ultra-thin La-BiFeO3 layer (< 10 nm) would lead to mixed 71° and 109° domain walls. In this protocol, thicker La-BiFeO3 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 BiFeO3/La-BiFeO3/SrRuO3/DyScO3 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 BiFeO3/La-BiFeO3/SrRuO3/DyScO3 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 films19. Using this technique, many investigations have been carried out on BiFeO3 thin films13, 20-22. As one of the most striking aspects, domain walls are widely studied due to a wealth of fascinating phenomena1-3, 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 electrode8, 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 BiFeO3 thin films by PLD, which indicates the significance with respect to existing methods8.

The PLD growth conditions (including laser energy, growth temperature, and oxygen pressure) of high-quality BiFeO3, La-BiFeO3, and SrRuO3 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-BiFeO3 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 BiFeO3/La-BiFeO3/SrRuO3/DyScO3 stack. Non-ferroelectric 25% La-BiFeO3 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 DyScO3—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 SrTiO3, LaAlO3, *etc.* cannot provide the required anisotropic strain.

Previous studies23 demonstrated that, due to the interplay between strain, depolarization field, and gradient energies, topological ferroelectric vortices can be produced in PbTiO3/SrTiO3 superlattices. The method shown in this protocol provides a possible application to explore the room-temperature multiferroic vortices in the BiFeO3 system. Furthermore, it can be used to control the ferroelectric polarization or domain structures in ferroelectric materials, such as BaTiO3 and PbZrxTi1-xO3.

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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 BiFeO3. *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 BiFeO3 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 BiFeO3 Thin Films. *Nano Lett.* **9**, 1726-1730 (2009).
9. Chen, Z. *et al*. 180° Ferroelectric Stripe Nanodomains in BiFeO3 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 BiFeO3 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 BiFeO3 thin films. *Nano Lett****.*** **8**, 2050-2055 (2008).
17. Bea, H. *et al*. Mechanisms of exchange bias with multiferroic BiFeO3 epitaxial thin films. *Phys Rev Lett*. **100**, 017204 (2008).
18. Chen, D. *et al*. Interface engineering of domain structures in BiFeO3 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 BiFeO3 multiferroic thin film heterostructures. *Science.* **299**, 1719-1722 (2003).
21. Zeches, R. J. *et al*. A Strain-Driven Morphotropic Phase Boundary in BiFeO3. *Science.* **326**, 977-980 (2009).
22. Huang, C. W., Chen, L. Effects of interfaces on the structure and novel physical properties in epitaxial multiferroic Bifeo3 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).