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ORIGINAL REPORT



Geometry confined polar vertex domains in self-assembled BiFeO₃ nano-islands

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ABSTRACT

Low-dimensional ferroelectric topological textures show abundant configurations such as flux-closure quadrants and vortices, suggesting potential applications in nano-electronic devices. However, the deterministic control of those polar textures is still challenging. By using piezoresponse force microscopy, threefold or fourfold vertex domain structures were observed in self-assembled BiFeO₃ nano-islands, and the formation of such polar topological textures is strongly dependent on the size and shape of the nano-island. Furthermore, the vertex domain textures confined by geometry can be reversibly switched back and forth by external electric field, which are stabilized by the competition between elastic energy and electrostatic energy.



IMPACT STATEMENT

Stable threefold or fourfold vertex domain structures are formed on BiFeO₃ nano-islands, depending on the size and shape of the nanoisland.

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KEYWORDS

Ferroelectric topological textures; BiFeO₃; self-assembled nano-islands; threefold/fourfold vertex domain

1. Introduction

Topological structures (e.g. domain walls, vortices) in ferroelectric materials have attracted intensive attention both for fundamental research and technological applications for non-volatile nano-electronic devices [1–4], since the performance of ferroelectric nano-devices is closely related to the domain structures and their stability to perturbation. Compared to the flux-closure quadrants [1,5] or vortex states [2,4,6] in ferroelectrics, vertex domains—the intersection between two or more domain walls in a ferroic materials—have not yet received much attention to date [7,8]. Actually, ferroelectric vertices exhibit many exotic properties, such as high electric conductivity [3,9], and creep process during vertex interaction [7]. Moreover, previous theory predicted that a pair of separated threefold vertices and a fourfold vertex would exhibit distinct stability, and the transformation

between these two types of topological domain pattern may be achieved by the coalescence or separation of the threefold vertex pairs [10]. These exciting discoveries sparked our interest in dedicating exploration of the vertex domains and the related responses against electric field in real cases, which is the prerequisite for the application of high density non-volatile electronic devices.

Ferroelectric nanoislands/nanodots are idea platforms to study the topological domain states owing to the constrained geometries or boundary conditions [11–19]. Recently, self-assembled BiFeO₃ (BFO) nano-island (about 200 nm × 200 nm) arrays have been successfully grown on LaAlO₃ substrate by pulsed laser deposition (PLD), and moreover center-type topological domains and charged domain walls with fascinating functional properties have been observed in the BFO nano-islands [3]. Considering rich domain structures

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in BFO thin films, this self-assembled BFO nano-island array provides us an excellent model system to study the topological domain configurations and the correlated dynamic evolution when exposed to electric field. The evolution of domain configuration in nanostructure is mainly determined by the stress field and depolarization field, while these two fields are directly related to the size of the nano-islands [11,15]. First, the strain state significantly changes due to strain relaxation at the edge and corner of the nano-islands. Second, the additional surfaces induce a special surface charge state, which directly influences the depolarization field of the island. Third, the geometry of the nano-island constraints the polarization structure [3]. All of these may effectively affect the elastic and electrostatic interaction energies, and thus the domain structures.

In this Letter, we report how the lateral size and shape of the nano-islands affect their polar domain structures. Our results reveal that the fourfold vertex domain structure [3] can spontaneously form in the square-shaped islands with lateral size less than ~ 590 nm, and general multi-domain configuration appear in larger islands; while in rectangle-shaped islands, a pair of separated threefold vertices rather than fourfold vertex domains form. Thus, there would be an upper limit size of ~ 590 nm for BFO nano-islands with the formation of such vertex domain configurations.

2. Experimental

BiFeO_3 nano-islands of about 40 nm in thickness were grown on (001) oriented LaAlO_3 single-crystal substrate by PLD as before [3]. $(\text{La,Sr})\text{MnO}_3$ (LSMO) films with thickness of 2–6 nm were deposited as the bottom electrode, at 700°C under 0.2 mbar oxygen pressure, with KrF excimer laser wavelength of 248 nm, repetition rate of 5 Hz, and energy density of ~ 1.5 J/cm². The growth conditions of BFO are the same as LSMO. After deposition, the samples were slowly cooled to room temperature in 200 mbar oxygen at a cooling rate of 10°C/min. Similarly to previous observations in ref. [3], the epitaxial BFO nano-islands with rhombohedrally distorted perovskite structure (R-phase) are self-assembled in tetragonally distorted perovskite matrix (T-phase).

Piezoresponse force microscopy (PFM) and atomic force microscopy (AFM) experiments on the BFO islands were performed at room temperature using an Infinity Asylum Research AFM. A tip with Pt/Ir-coated Si cantilever (tip radius of 20 nm, force constant of 2.8 N/m, and a resonant frequency of 75 kHz) was used as a movable top electrode to apply bias voltages. Both the vertical and lateral PFM were conducted at different in-plane sample rotation angles to reconstruct the 3D domain

structures. The PFM signal was collected at the contact resonance frequency with AC tip bias of 1 V.

3. Results and discussion

1. At appropriate growth conditions, rectangle- and square-shaped R-phase BFO nano-islands with various sizes can self-assembly formed and embedded in T-phase BFO matrix [3]. In order to determine the domain structure on the BFO islands in detail, high-resolution angle-resolved PFM measurement was performed. Figure 1 shows the characterization process for an example on a square-shaped island of 400 nm $\times$ 400 nm. Out-of-plane (OOP) PFM phase image in Figure 1(a) shows an upward polarization projection for the quad-domain. To determine the in-plane (IP) polarization variants of the nano-island, the cantilever was placed parallel to [100] (Figure 1(b)), [110] (Figure 1(c)), [010] (Figure 1(d)), and $[\bar{1}10]$ (Figure 1(e)) orientations of the substrate, respectively. The bright and dark PFM phase contrast in Figure 1(b–e), as well as corresponding schematics in Figure 1(g–j), indicates that the IP components of the polarization are antiparallel and both are perpendicular to the cantilever. While the intermediate contrast suggests the IP polarization components are parallel to the cantilever. Combining the OOP and IP polarization components, the three-dimensional (3D) domain structure can be constructed, i.e. a center-type quad-domain configuration (vertex-like) [3] with 71° charged domain walls, as shown in Figure 1(f).

By systematically exploring the domain configurations of the nano-islands with different lateral sizes, we discovered that the domain configurations are dependent on the lateral size of the nano-island, as seen from Figure 2. A general multi-domain structure (Figure 2(a)) appears on the 750-nm island, where both the OOP and IP phase images are divided into many parts to reduce the depolarization field [8]. While on 400-nm island, a quadrant domain configuration with cross-shaped fourfold vertex (Figure 2(c)) is emerging, as observed in small nano-islands of less than 200-nm [3], which is attributed to the degradation of substrate clamping and strengthen of depolarization field effect. Interestingly, in comparison with the 400-nm (or smaller [3]) island, the quadrant domain structure is broken by additional domain walls for the 600-nm island (Figure 2(b)), indicating that there may be a critical size for the formation of quadrant domain configuration with a fourfold vertex.

In order to understand the size effect, we assume that such a quadrant domain configuration with a fourfold domain wall vertex is the ground domain state. Formation of an additional domain wall above a certain

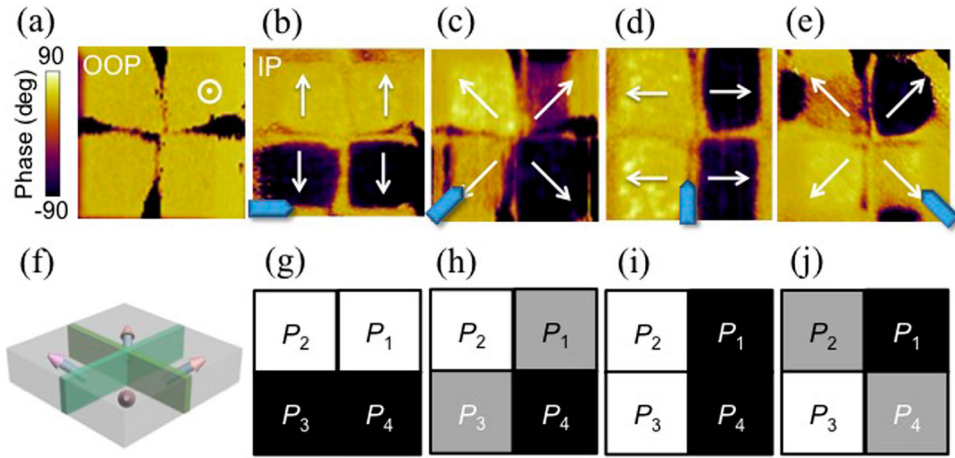


Figure 1. PFM characterization process for domain structures on BFO nano-islands. (a) OOP domain of a 400 nm square-shaped BFO nano-island. The IP domain is determined by characterizing the polarization at (b) 0° (with the cantilever parallel to the $\langle 100 \rangle$ crystallographic direction), (c) 45°, (d) 90°, and (e) 135°. (f) 3D schematic diagram of the domain structure of BFO nano-island. (g)–(j) Schematics of the corresponding domain structures to (b)–(e). The white arrows indicate the IP polarization directions. The blue arrow indicates the schematic diagram of the cantilever.

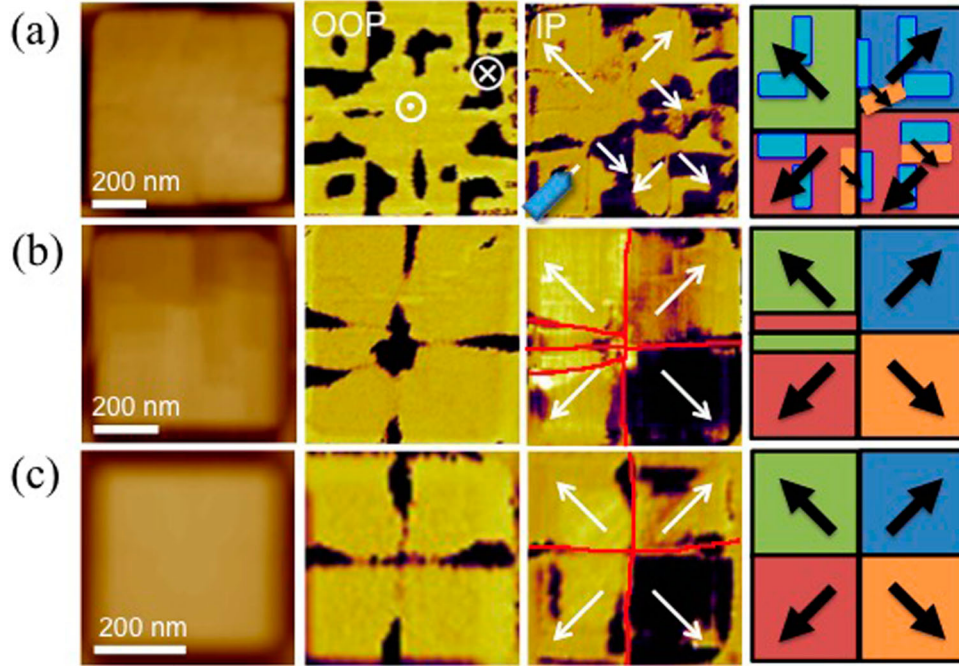


Figure 2. Domain configurations of square-shaped BFO nano-islands. Shown from left to right are respectively the morphology, OOP phase image, IP phase image, and schematics of IP domains for BFO islands with lateral size of (a) 750 nm $\times$ 750 nm, (b) 600 nm $\times$ 600 nm, and (c) 400 nm $\times$ 400 nm. The red lines schematically denote the domain walls. The white and black arrows indicate the IP polarizations. The blue arrow indicates the schematic diagram of the cantilever. In the schematics of (a), the small blue rectangles represent domains with out-of-plane downward polarization, while other areas with upward polarization.

critical size would alleviate the associated stress and break the quadrant configuration [8]. When the elastic energy in a single quadrant domain equals to the energy cost of an additional domain wall, the critical size could be determined. The dimensions of the square-shaped nano-island can be regarded as Width $\times$ Width $\times$ height ($W \times W \times d$). The elastic energy density stored in a

quadrant of volume $W^2d/4$ can be given simply by [8]

$$E_{\text{elastic}} = \frac{1}{2} G s^2 \frac{W^2 d}{4}, \quad (1)$$

where G is the elastic shear modulus and s is the elastic strain. The energy cost for the formation of an additional

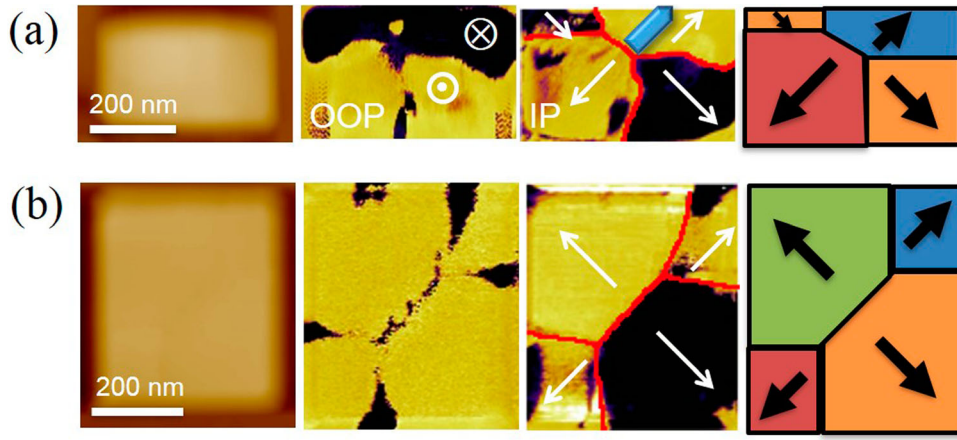


Figure 3. Domain configurations of rectangle-shaped BFO nano-islands. Shown from left to right are respectively the morphology, OOP phase image, IP phase image, and schematics of IP domains for BFO islands with lateral size of (a) 200 nm × 400 nm, (b) 400 nm × 500 nm. The red lines schematically denote the domain walls. The white and black arrows indicate the IP polarizations.

wall is given by [8]

$$E_{\text{wall}} = \sigma \frac{1}{2} Wd, \quad (2)$$

where σ is the surface energy density of the wall, and Wd is the area of the new domain wall. If $E_{\text{elastic}} = E_{\text{wall}}$, then the critical size of the nano-island with a fourfold vertex domain can be determined as

$$W = 4 \frac{\sigma}{Gs^2}. \quad (3)$$

For the case of BFO, $G = 30$ GPa [20], $\sigma = 0.44$ J/m² [21], and s is about 0.01 [8], and thus the critical size could be approximately 590 nm or less. This simple analysis is in agreement with the above experimental observations.

In addition to the size effect above, the shape of the nano-island also has a significant effect on the domain structures. As seen from Figure 3(a), on the rectangle-shaped nano-island of 200 nm × 400 nm, a pair of asymmetric threefold domain-wall vertices appear. It is worth to mention that a pair of threefold vertices could be regarded as a fourfold vertex that separated at its center [8]. When the shape of the nano-island changes from square to rectangle with shrinking one side, the symmetric fourfold vertex would bifurcate into two threefold vertices to decrease the total energy. As seen from Figure 3(b), even in the nearly square-shaped 400 nm × 500 nm island, a pair of threefold domain-wall vertices rather than a fourfold vertex also arise. With increasing the aspect ratio of the island, the domain structures become quite complicated due to the serious distortion of the vertices on the large rectangle-shaped islands, e.g. 200 nm × 700 nm (not shown here).

To further explore the stability of the vertex domain configurations when exposed to an external electric field, ± 4 V probe voltage (larger than the coercive field) was applied on the nano-island with respect to the bottom LSMO electrode. Consistently with our previous observations on 200-nm square-shaped nano-islands (Figure 3 in ref. [3]), the fourfold vertex domains in all square-shaped nano-islands can be reversibly switched between center-divergent and center-convergent quad-domains under ± 4 V electric field, i.e. fourfold vertex quad-domains on the square-shaped nano-islands are topologically protected and stabilized [3].

Similarly to the fourfold vertex, it can be found that the domain structure with a pair of threefold vertices (Figure 4(a,b)) is also quite stable under the applied electric field. As shown in Figure 3(b), the island initially exhibited a pair of threefold vertices domain with OOP polarizations upward and IP polarizations outward. After applying a +4 V voltage on the nano-islands by the scanning probe (Figure 4(a)), the OOP polarization direction was switched from upward to downward, and the IP polarizations pointed to inward, which indicates a 180° switching of the polar vectors. When applying a −4 V voltage on this island by the scanning probe (Figure 4(b)), the polar vectors switched 180° once again, and both the OOP and IP polarizations switched back to the initial state. Thus, this domain structure with pairs of threefold vertices can be switched back and forth by electric field between the two stable states with pairs of threefold vertices, i.e. center-convergent vertices and center-divergent vertices. The switching process implies that the polar texture with a pair of threefold vertices are also stable as the cross-shaped fourfold vertex domains, which is different

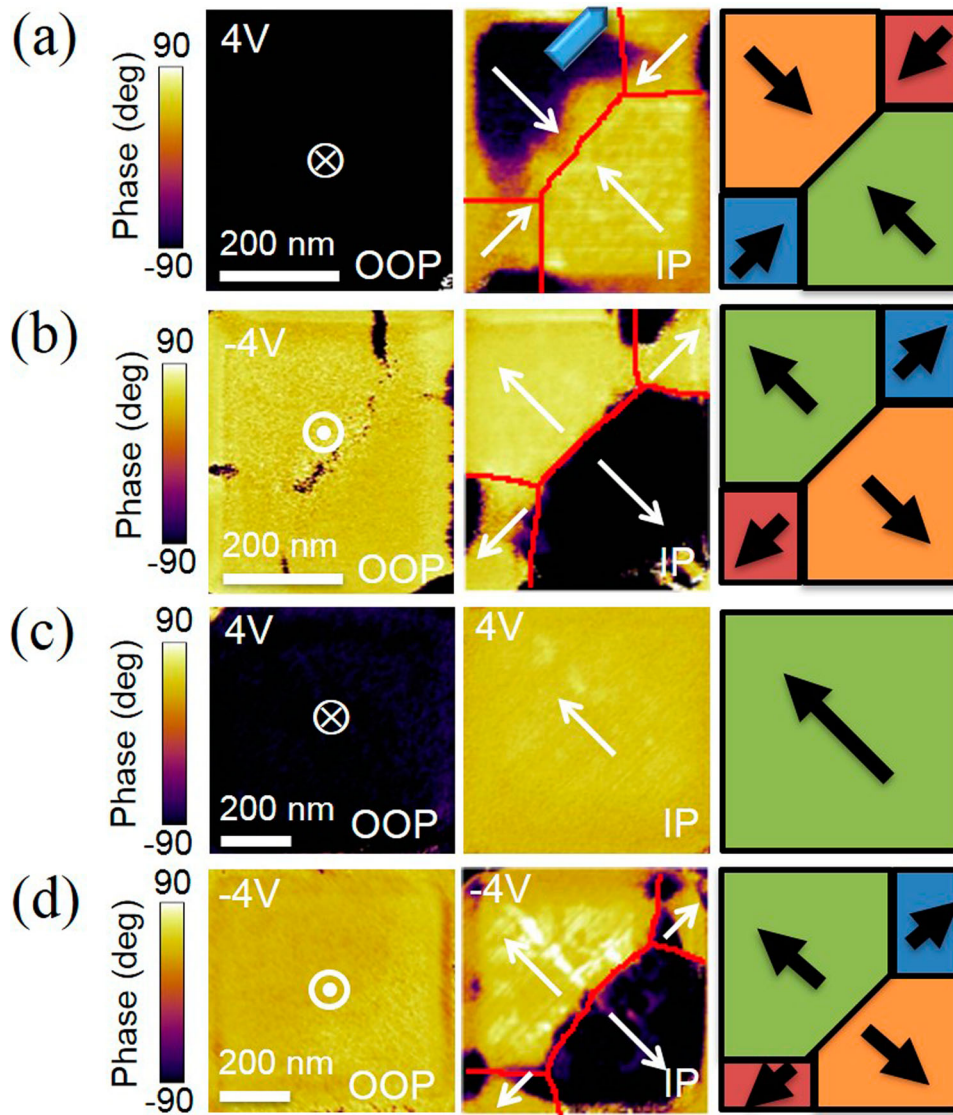


Figure 4. Domain switching of BFO nano-islands with lateral size of (a,b) $400\text{ nm} \times 500\text{ nm}$, and (c,d) $700\text{ nm} \times 700\text{ nm}$, respectively. For each figure from left to right, the three images are OOP and IP phase under $+4\text{ V}/-4\text{ V}$ electric field, and schematics of IP domain wall vertex, respectively. The red lines schematically denote the domain walls. The black and white arrows indicate the IP polarizations. The blue arrow indicates the schematic diagram of the cantilever.

from the calculated results [8], where coalesce or separation of the pairs of threefold vertices would occur. This is probably due to the strong geometry confined effect in the BFO nano-islands.

For a $700\text{ nm} \times 700\text{ nm}$ large island, the initial multi-domain structure totally changed after a $+4\text{ V}$ voltage was applied on the island by the scanning probe (Figure 4(c)). Both OOP and IP polarization components point to one direction, implying a mono-domain state. When a -4 V voltage was applied on the island by the scanning probe (Figure 4(d)), the domain structure surprisingly varied to a pair of asymmetric threefold vertices, but the relative area of the four parts is different, indicating a distorted vertex domain configuration. However, when repeatedly applying $\pm 4\text{ V}$ voltage to the island,

the domain structure changes each time, indicating an unstable domain state when exposed to external electric field.

4. Conclusion

In summary, the domain structures with the cross-shaped fourfold vertex or pairs of separated threefold vertices have emerged on self-assembled square-shaped or rectangle-shaped BFO nano-islands, respectively, with an upper limit size of about 590 nm , which are mainly determined by the competition between elastic and electrostatic energy. Both domain structures are topologically protected and stabilized, and thus can be switched back and forth between convergent and divergent vertex

states. The charged domain walls in the nano-islands with topological vertex domain structures imply the potential applications in ferroelectric nano-devices with robust stability [3].

Disclosure statement

No potential conflict of interest was reported by the authors.

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