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Hierarchical-vortex polarization domain pattern in nano polycrystalline ferroelectric

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Domain pattern is the carrier of electromechanical property. A novel domain pattern will open a gate for ferroelectric nanodevice. A distinctive topological domain pattern termed as hierarchical vortex (Hvo) has been found in polycrystalline ferroelectric based on the first-principles-based atomistic method. The Hvo pattern displays a unique structure, which is a flux-closing vortex encircle an anti-vortex or a vortex and anti-vortex pair (VA). Each Hvo structure could be regarded as a single vortex to forming a vortex–anti-vortex pair with anti-vortex or forming a vortex–vortex array with the vortex. The mechanism of HVo obtained in polycrystalline ferroelectric has been found that the grain boundary (GB) equals the domain wall when the first-order vortex is in the vortex. The HVo will open a new view of the domain topology pattern and its evolution.

Keywords: Domain pattern; hierarchical vortex; polycrystalline; grain boundary; self-consistent.

Ferroelectric materials display a remarkable range of phenomena that can be influenced by the formation of nanostructures or nanoscale interfaces.[1–4] The polarization domain is the media of the distinguished electromechanical property of ferroelectric.[5–7] A novel domain pattern will open a new gate of applications in micro/nano device. Recently, the study of domain configuration focuses on the vortex domain and its new topological version vortex.[8–12] The vortex domain is a novel polarization domain structure found in the ferroelectric films. Vortex has been predicted that it offers the possibility of high-density memory (Tb/in2) and storage with electrical write (fast) and magnetic read (no reset).[13]

To the best of the authors' knowledge, four typical topology structures about vortex-like have been found, i.e., (a) Vortex, (b) Anti-vortex, (c) Vortex–vortex array and (d) VA pair, which are shown in Fig 1. Signatures of polarization vortex state in ferroelectric have been studied by theoretically[8–11,14] and experimentally.[15–17] The vortex pattern has been predicted to be the high-density memory. Compared with the vortex, an in-plane anti-vortex is defined as a domain arrangement where a pair of polarization components point toward each other and another pair point away from each other.[18–20] The anti-vortex domain structure has been observed in epitaxial $BiFeO_3$ thin film.[21] This anti-vortex pattern has changed the vortex evolution preceding, which could annihilation with vortex during the vortex evolution.

The vortex–vortex array is a classical vortex composite structure, which is formed by several vortexes with different orientations. Different orientations of vortex pairs have been first predicted by Naumov using simulations in ferroelectrics,[8] which is opening the gate of vortex structure.[10,22,23] Now, those topology structures can be directly observed not only as the atomic morphology of the flux-closure quadrant but also a periodic array of flux closures in $PbTiO_3$ films.[24] The vortex–vortex array is related with the interface[25] and defect.[26] Pattern D is a VA pair formed as the polarized vortex domain accompanying a polarized anti-vortex domain in ferroelectric materials.[27–29] According to the experimental observations by Ivry *et al*.[30] and the atomic simulations by Tian *et al*.,[31] the polarized vortex and anti-vortex domains in ferroelectric materials could move relative to one another, colliding and annihilating under certain conditions.

All those four topology domain structure patterns of the flux-closing vortex are found in the form of a single crystal. But most of the ferroelectric films employed in the industry are polycrystal. In polycrystalline ferroelectrics, the GB,[32,33] grain size[34] and grain orientation[35] can change the domain distributions.[36,37] Therefore, are there some interesting and new patterns caused by the grain orientation and GB effect in polycrystalline ferroelectric which are widely used in industry? This study will give a positive answer. In this work, a novel topology domain structure termed as hierarchical

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vortex (Hvo) has been obtained in polycrystalline ferroelectrics by first-principles-based atomistic simulation with the shell model.

An anisotropic shell model potential has been successfully applied to investigate electromechanical coupling responses[38] and the reproduction of vortex in $PbTiO_3$ nanoparticles[9] and $BaTiO_3$ (BTO) nanofilm.[31] This work applied the same model based on DL_POLY package frame.[39] The potential parameters can be obtained from the first principle calculations. The calculation details, as well as the related parameters, can be found in the literature.[31] In this simulation, the BTO polycrystal consists of twelve hexagon grains with 10 nm in diameter and 2.4 nm in height (Fig. 1(a)). Each hexagonal grain has a different orientation and the GB is formed due to the different grain orientations. The crystallography axis of grain rotates only in the x–y plane. The local coordinate axes are shown in each grain with labels from 1 to 12 corresponding to different orientations. The atomic position on the GB or the GB width is determined by the grain interaction which can be changed under external force fields and external constrains. Periodic boundary conditions are imposed on all surfaces of the model and electric boundary conditions on all sample surfaces are open-circuited. The temperature is set as 2.5 Kelvin near-absolute zero[31] and particles are still active and can move easily to proper positions. Figure 2(a) shows the atomic structure in polycrystalline ferroelectrics. In this figure, each arrowhead with color represents the polar of one lattice. The polarization is calculated based on lattice cell.[31,38] Taking the Ti-center cell, for example, the polarization component in the α direction for unit cell m is defined[40] as follows:

$$p_{\alpha m} = \frac{1}{V_m}\left(\sum_i \sum_{n=1}^{2} q_{inm} r_{in\alpha m}\right), \qquad (1)$$

where V_m is the cell volume and q_{inm} and $r_{in\alpha m}$ are the charge and coordinate along the α direction, respectively. For given

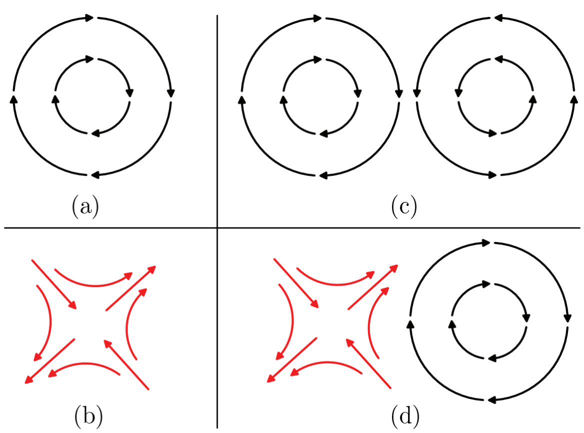

Fig. 1. The scheme of domain pattern: (a) Vortex, (b) Anti-vortex, (c) Vortex–vortex array and (d) VA pair. Topology structures are comprised by VA pair.

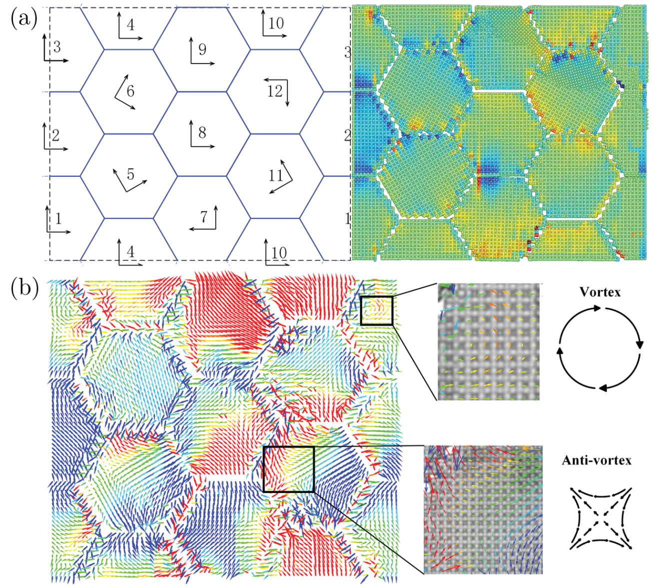

Fig. 2. (a) The atomic structure of polycrystalline $BaTiO_3$ Nano-film composed by 12 grains at atomic scale. (b) The polarization configuration with single vortex and anti-vortex. A scheme of the topological domain structure of the vortex and anti-vortex is shown at the right side. The color represents the angle of the vector along the *x*–*y* axis.

particle *i*, *n* = 1 and 2 correspond to the core and shell, respectively.

In order to clearly understand the domain pattern, the polarization configuration with single vortex and anti-vortex has been obtained in this work, as shown in Fig. 2(b). The stream of the vector with atomic background exhibits the vortex at grain 1 and anti-vortex at grain 11. A scheme of the topological domain structure of the vortex and anti-vortex is shown on the right side in Fig. 2(b). It should be mentioned that some special domains such as the 90-degree domain and the anti-vortex can only be obtained in a single grain in opening literature,[10,11] but our simulation results show that some novel topology domain structures could also be found from the whole picture of grains.

Figure 3(a) shows the contour map of the polarization values. It can be found that the polarization values at the grain boundary (GB) are larger than those inside the grain. Although the values at the GB are disorder, there are six obvious ordering areas, which exhibit a circular contour in a grain. A circular contour area means that there may be anti-vortex domain structure. Figure 3(b) gives the marks of the ordering areas as A_1–A_6. As shown in Fig. 3(c), vortex V_1 is formed at GBs, involving grain numbers 3, 4 and 6. Vortex V_2 is combined by a series of domains in which an arrow is used to connect the head and the tail of the polarization vectors that manage to attain flux closure as a vortex. Vortex V_2 involves grains 2, 4, 5, 6, 9, 10, 11 and 12. Although all these grains have different polarization distributions, the polarization distribution between their neighborhood grains maintains

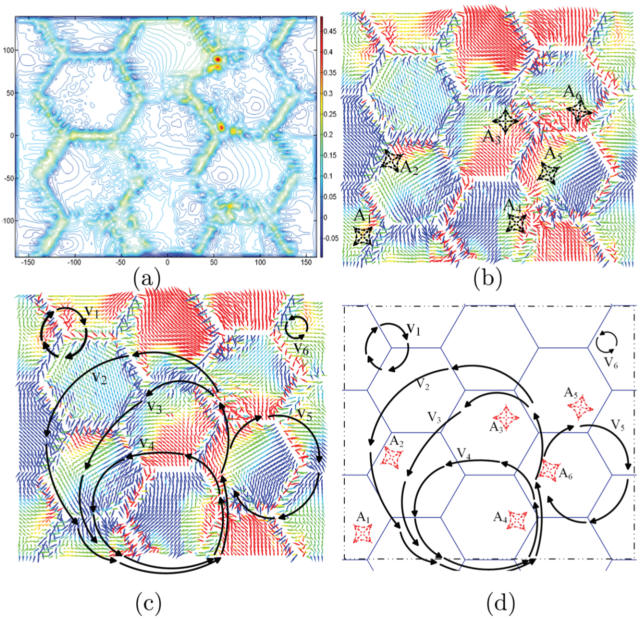

Fig. 3. (a) The contour map of the polarization. (b) Anti-vortex, which obtained in polarization configuration. (c) Scheme of vortex with polarization configuration. (d) Scheme of topological domain structure of the vortex and anti-vortex combined with GB in ferroelectric polycrystal. The hexagon represents the grain and GB, and the vortex and the anti-vortex are marked as the letters V and A with subscript number.

continuum without any obvious domain wall except at the GB which locates at between grains 9 and 6. The continuous distribution across the different grains has been confirmed in the experiment for polycrystalline ferroelectrics,[41] the phase-field simulation for the grain orientation effect[35] and grain size,[34] and the domain continuity over GB.[32] The domain walls in vortex are formed by about 90-degree domains, which is similar to Ivry's experimental observation.[42] The vortex V_3 involves grains 4, 5, 6, 8, 10, 11 and 12. Similarly, the polarization is continuous at all GBs. The vortex V_4 in this simulation involves grains 4, 5, 7, 8, 10 and 11. The domain between grains is like the vortex V_3. Vortex V_5 involves grains 10, 11, 12, 1 and 2, and Vortex V_6 is located at grain 3. Those single vortex and anti-vortex distributions are in good agreement with the single crystalline ferroelectric which has been obtained in experiments[38] and simulations.[11]

Four patterns of domain structures can be obtained in this simulation by comparing Fig. 3(d) with Fig. 1. The vortex which marked as V_6 is corresponding to pattern A. The anti-vortexes A_1 to A_6 could be pattern B in Fig. 1, and pattern C can be found to be V_5 and V_2. Except for A_6 and V_6, all vortexes marked with A and V for the anti-vortex and the vortex can be seen as pattern D. This pattern passes through different grains in this work, and it can be obtained in polycrystalline ferroelectrics. These vortexes also maintain the rule of forming the vortex–vortex pairs or VA pairs. This result gives direct evidence that patterns C and D not only exist in single-crystalline ferroelectrics but also in polycrystalline ferroelectrics.

Except for the four patterns of domain structures, a new pattern of the topological structure has been found in this simulation. This novel domain structure, i.e., V_4 which contains an anti-vortex A_4, can be seen in Fig. 3(d). In addition, anti-vortex A_4 is encircled by the vortex V_4; vortex V_4 and anti-vortex A_3 are encircled by the vortex V_3; vortex V_3 and anti-vortex A_2 are encircled by the vortex V_2, and vortex V_2 and anti-vortex A_1 can be seen as the pattern D domains. Although domain structures can be formed by vortexes and anti-vortexes, it does not in the form of one circling another. In Prosandeev's study,[14] an evolution process presents part of Hvo pattern. Therefore, it can be confirmed that a novel topology domain structure appears.

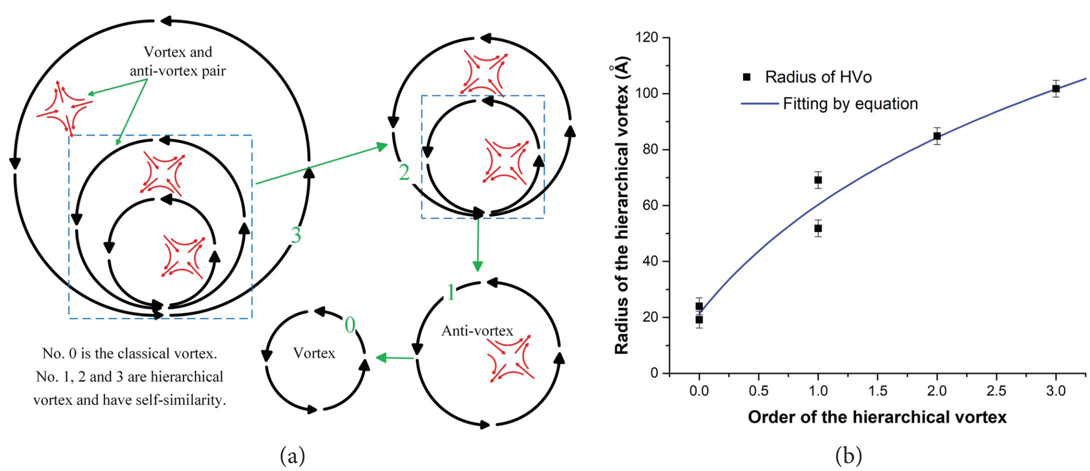

Fig. 4. (a) Scheme of the Hvo. No. 0 is the classical vortex. Nos. 1, 2 and 3 are Hvo with self-similarity from No. 1 to 3. The Hvo can be formed a VA pair with a neighbor anti-vortex. The cross scheme represents the anti-vortex. Each dashed line box of the higher-order Hvo is the lower-order Hvo. (b) The radius of the Hvo is corresponding to different orders of the Hvo. Each order of the Hvo has been schemed by the vortex and anti-vortex.

This novel domain structure is termed as Hvo (hierarchical vortex) domain because of the unusual pattern. The Hvo is defined as a vortex domain formed by a flux-closing vortex domain, as shown in Fig. 4(a). There are three orders of the Hvos. No. 0 is the classical vortex, and Nos. 1, 2 and 3 are Hvos with self-similarity from Nos. 1 to 3. The No. 1 Hvo is formed by a vortex which encircles an anti-vortex, corresponding to V_4 and V_5. This topology structure of the vortex is defined as the first order Hvo because of only one stratum. The Hvo can form a VA pair with a neighbor anti-vortex as V_5 and A_5 are shown in Fig. 3. The second Hvo is formed by the first order as the No. 2 Hvo shown in Fig. 4(a), which corresponds to V_3 in Fig. 3(d). The boundary of the No. 2 Hvo is a vortex and inside contains a VA pair which is the first order Hvo and anti-vortex. Expanding the Hvo with No. 2, the third-order Hvo is vortex which encircles the second-order Hvo and anti-vortex, which corresponds to V_2 in Fig. 3(d). The third-order Hvo is like the forming of the second-order Hvo.

Three special properties of the Hvo have been found. One property is the shape of this domain structure, which is similar to the vortex, as shown in Fig. 4(a). The second property is that each order of the Hvo can form a vortex–anti-vortex (VA) pair. To encircle a VA pair, the Hvo domain must exist in polycrystalline ferroelectric due to the GB interrupts the inerratic of the domain structure. The GB can be equal to the domain wall.[32] The domain wall is the polarization field above the lattice level. At the lattice scale, the GB in polycrystal is a discontinuity naturally. Then, this discontinuity of the Hvo inside is easy to occur for the polycrystalline because of the GBs. Hence, it can be concluded that the situation of the Hvo structure formed must contain a key element, i.e., polycrystalline ferroelectric. That is the reason why the Hvo has not been observed in experiments. This result could give guidance to observe the domain structure in ferroelectrics.

The third and important one is the self-similar property of the Hvo domain structure. The self-similarity of the Hvo is that each higher-order Hvo contains the lower-order Hvo and anti-vortex. The higher-order Hvo circling a VA pair, which is combined with the lower-order vortexes and the anti-vortexes. Then, the radius of the Hvo is growing bigger because of the self-consistent property. These radii have been obtained in Fig. 4(b), where order 0 is V_6, and orders 1, 2 and 3 are corresponding to V_4, V_3 and V_2, respectively. The radius of the Hvo can be estimated as the following relationship

$$R \propto \ln(n), \qquad (2)$$

where n is the order of Hvo. The fitting equation has been estimated as $R = 11 + 63 \ln(A + 0.18)$. This equation has a good agreement with the observation value of the Hvo at different orders in this study from Fig. 4(b).

The Hvo possesses the special domain structure combined with GBs in contrast to vortexes or anti-vortexes. As the forming mechanics of the Hvo, four Hvo patterns are

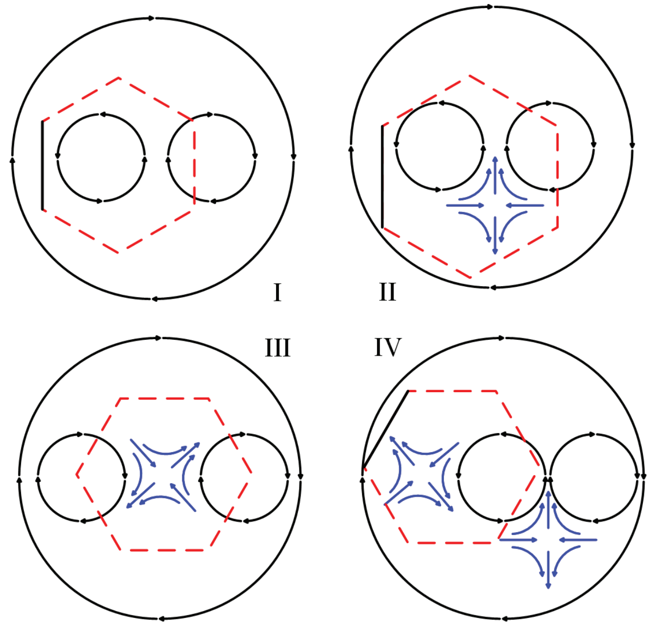

Fig. 5. Four domain patterns combining with grain and GB can be predicted from the generating mechanism of Hvo. The pattern I is vortex–vortex and GB. Pattern II is the vortex–anti-vortex–vortex with GB. Pattern III is the vortex–anti-vortex–vortex with GB. Pattern IV is more complicated vortex pattern. The red hexagon represents the grain and GB.

being predicted shown in Fig. 5. Those domain patterns are combined with grain and GBs. It indicated that polarization domain patterns need more attention in polycrystalline ferroelectric because of GBs. The domain evolution and electromechanical response are more complicated and more interesting because of GBs.[43] Domain wall continuity across grain boundaries has been observed since the 1950s. The relationship between the different orientation GBs and domain wall continuous has been found by Mantri.[32] For Hvo structure, there must contain some GBs. The GBs can be the domain wall to maintain the discontinuation inside the Hvo. This is the defect of the structure and domain wall work together to form the Hvo domain structure. The Hvo has been forming as a vortex encircling the vortex and anti-vortex pair. On the anti-vortex side, the Hvo structure will have some discontinue on the anti-vortex streamlines. The reason why the Hvo only can be observed in polycrystalline ferroelectric because of the GBs. Those patterns could bring many interesting phenomena for domain patterns and novel applications for the design of ferroelectric devices. Vortex has been predicted that it offers the possibility of the high-density memory and storage with electrical write and magnetic read by an applied electric field. This vortex pattern can be stable based on grain structure without an external field applied. It will be easier for controlling of the domain configuration and domain dynamic behavior when designing for devices. On the other hand, this pattern also opens a gate for behavior controlling based on the structure and strain engineering.

In conclusion, this study reports an unusual topological domain structure in polycrystalline ferroelectric. The Hvo possesses a self-consistent property which can ensure the formation of a pair of a vortex and an anti-vortex. This new finding may turn the research's attention to designing domain patterns by GB engineering. The domain evolution and electro-mechanical response are more complicated and more interesting because of GBs. Some further questions arise about the Hvo, i.e., how this structure affects the electromechanical response under electrical or mechanical loadings? How can the vortex and anti-vortex in Hvo structure migrate and annihilate with each other? How does the GB affect the formation of the Hvo? Once all these issues have been addressed, the Hvo could bring much more interesting phenomena and many novel applications for the ferroelectric device design.

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