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Self-organization nanodomain structure in ferroelectric ultrathin films

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Abstract
Through *ab initio*-based simulations of the perovskite ferroelectric ultrathin films, we find that on applying an external electric field, ferroelectric ultrathin films can form kinds of self-organization nanodomain patterns including concentric loop stripes and nanodomain lattices. The characteristic size of the domain structure can be conveniently adjusted by controlling the film thickness and field, which should be very attractive in many applications. Our results are helpful for understanding the difference between the ferroelectric ultrathin film and bulk.

Ferroelectric materials are characterized by multi-stable states with differing spontaneous polarization. These multi-stable states can coexist in ferroelectric material, forming domain structure. Some special ferroelectric domain patterns have been found to be very important to modern technology. For example, the periodic 180° stripe is very useful for implementing quasi-phase matching in nonlinear ferroelectric optical material [1–3]. Ferroelectrics with the two-dimensional ordered domain structure (such as nonlinear photonic crystals) provide a valuable platform for studying light–matter interaction in a highly nonlinear regime [4–7]. Recently, the ferroelectric nanodomain pattern has been found to be very useful for assembling dissimilar nanostructures [8, 9]. Kalinin *et al* [8] reported that the complex multicomponent nanostructures can be assembled directly by manipulating atomic polarization in ferroelectric substrates to control local electronic structure and influence the chemical reactivity. Therefore, how to form the useful domain pattern becomes a very critical issue. Several methods, such as the chemical in-diffusion [10, 11], the electric field poling method [12, 13], electron beam methods [14] and writing directly with the probe tips, have been developed for producing the special domain patterns. However, it is rather difficult or inefficient to produce nanosize domain patterns [13] by these methods. It will be very attractive if ordered nanodomain patterns can be formed via self-organization in the ferroelectric materials.

Recently, many observations revealed an equilibrium polydomain (namely, a self-organization domain structure) in ultrathin film or other nanostructure. Drezner and Berger observed multidomain structures having 180° and 90° domain boundaries in 2–7 nm thick $BaTiO_3$ films by using high resolution transmission electron microscopy [15]. A monodomain to polydomain transition in $PbTiO_3$ thin films has been demonstrated via piezoresponse atomic force microscopy measurements [16]. A 90° domain with in-plane polarization was found in ultrathin lamellae and nanocolumns of $BaTiO_3$ [17, 18]. 180° stripe domains with the period of several nanometres in ultrathin film have been observed with x-ray study [19, 20] and simulated using an *ab initio*-based approach [21–23]. The electric field can obviously influence the ferroelectricity [24]. However, it is still unknown how these ferroelectric polydomain evolve under the external field and whether new domain structure will form. Furthermore, a new ferroelectric off-centre displacement pattern with vortex structure in nanodiscs has been disclosed by *ab initio*-based simulation [25–29]. This strongly supports the belief that low dimensional structure such as ferroelectric ultrathin films will exhibit some ferroelectric properties distinctly different from those of bulk materials since the ferroelectricity is a collective phenomenon. Then what is difference in ferroelectric response to the electric field between ultrathin film and bulk material?

Here we report *ab initio*-based simulations carried out to investigate the effect of external electric fields on periodic stripe domains in ferroelectric ultrathin films. We observe two transformations of the domain structure, which indicate a domain evolution completely different from that of bulk material. Firstly, the straight stripes transform into concentric loop stripes in the field region. Then with increasing field, the concentric stripes further transform into a nanodomain lattice. The order and disorder distributions of Zr and Ti atoms influence the order of the nanodomain lattice. The characteristic size of the domain structure can be conveniently adjusted by controlling the film thickness and the external field, which is very attractive in many respects such as regards nonlinear photonic crystal and the assembly of nanostructure.

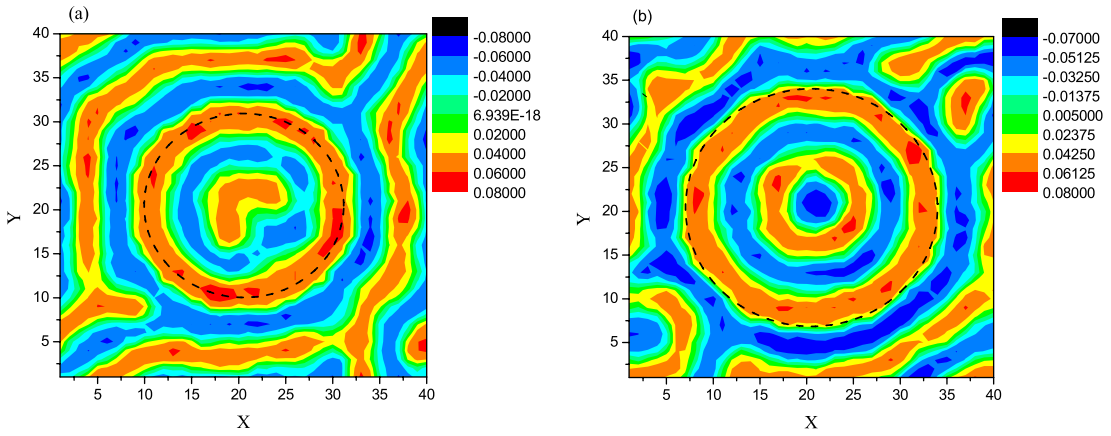

Figure 1. The out-of-plane polarization of the $40 \times 40 \times 4$ supercell. A local external field of $E = 3 \times 10^7$ V m^{-1} is applied to a region (indicated by a dashed line) with the diameter of (a) 21 and (b) 28 unit cells.

The system that we investigated is the $Pb(Zr_{0.5}Ti_{0.5})O_3$ (PZT) ultrathin films without charge screening. We adopt the effective Hamiltonian of PZT alloys proposed by Bellaiche, Garcia and Vanderbilt [30, 31], which is derived from first-principles calculations, to determine the ferroelectric off-centre displacement in each perovskite five-atom cell. The simulation based on the above Hamiltonian reproduced well the observed thermodynamic behaviour of bulk PZT, including the occurrence of an unusual monoclinic phase for a small range of Ti composition [30]. The influence of the substrate is imposed by confining the homogeneous in-plane compressive strain. Namely, $\eta_1 = \eta_2 = 2\%$ and $\eta_6 = 0$. The effect of the external field is considered by adding the term $-E\sum_i p_i$ in the Hamiltonian, where p_i is the dipole of the ith unit cell in the region of the field. The field is exerted along the growth direction of the film in two ways: one is that the global field is homogeneously applied to the whole film; the other is that the local field is exerted only on a part of film, simulating the effect of the field produced by the metallic tip of a microscope. Due to the periodic boundary adopted in the film plane, the local field appears periodically, similar to the field created by the array of the tips. The details of our approach for ultrathin film are described elsewhere [21]. The validity of the approach for ultrathin films was demonstrated by the fact that the calculated critical thickness [21] and 180 stripe domain [21, 22] are highly consistent with the x-ray observation [19, 20].

Our previous work demonstrated the existence of the periodic out-of-plane 180° straight stripe domains in the PZT films under 2% compressive strain for films with thickness larger than four unit cells [21]. When a local field was applied to the film, we found that the straight stripes transformed into a series of concentric loop stripes in the field region. An example for a film with the thickness of four unit cells is shown in figure 1. The loop stripe also has almost the same width as the straight stripe under zero electric field. The number of loop stripes changes with varying size of the local field region. Figures 1(a) and (b) respectively indicate three loop stripes and four loop stripes in the field region where the diameters of the local field are respectively 21 and 28 unit cells. It can be seen that the polarization of the outermost loop stripe in the field region is always parallel to the field. When a new loop stripe is formed with increasing diameter of the local field region, the direction of the polarization of each primary loop stripe will reverse. This can be clearly seen in figures 1(a) and (b), where the corresponding loop stripes have opposite out-of-plane polarization. The direction of the domain in the centre of the field region is along the direction of the external field in figure 1(a) but is antiparallel to the field in figure 1(b). It is interesting to note that the polarization of any loop stripe can be alternately reversed by increasing the diameter of local field region, which might be implemented by changing the distance between the tip and film.

We observe another domain transformation when the field is further enhanced. Figure 2 shows the domain structures with different field strengths. The broadening of the stripe along the field and narrowing of the stripe antiparallel with the field are not obvious when the field strength changes from $E = 3 \times 10^7$ V m^{-1} (figure 1(b)) to $E = 12 \times 10^7$ V m^{-1} (figure 2(a)). This indicates that the stripe domain wall is hardly shifted under an external field. Generally, it is expected that when the applied electric field increases, the antiparallel stripe domain will monotonically shrink and finally disappear. However, we found that the case for ultrathin film is different. When the field strength further increases, the structure of a series of concentric loop stripes is destroyed and many nanodomains with antiparallel polarization appear in the field region (figure 2(b)). These nanodomains show a tendency to close packed arrangement.

In order to further investigate the structure formed by nanodomains, we also study the case where the field is applied to the whole film. In this case the straight stripes transform directly into a structure composed of nanodomains. This is because the concentric loop stripe is not compatible with the periodic boundary adopted in the simulation. The distribution of nanodomains is strongly influenced by the ordering of the Zr and Ti atoms in the configuration. The nanodomains will form the ordered domain lattice if the PZT film is completely ordered. As shown in figure 2(b), the nanodomains tend to be close packed, and the hexagonal nanodomain lattice is expected to be formed. However, because the perfect hexagonal nanodomain lattice is incompatible with the tetragonal supercell and periodical boundary condition used, the hexagonal nanodomain lattice in our simulations is a little distorted. Figure 3(a) shows the distribution of nanodomains

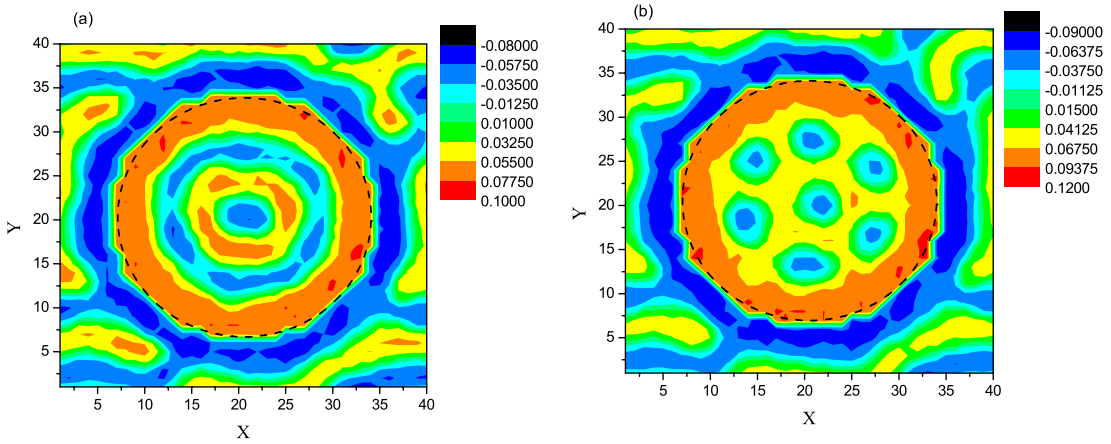

Figure 2. The out-of-plane polarization of the $40 \times 40 \times 4$ supercell under different field strengths: (a) $E = 12 \times 10^7$ V m^{-1} and (b) $E = 24 \times 10^7$ V m^{-1}. The external field region with the diameter of 28 unit cells is indicated by a dashed line.

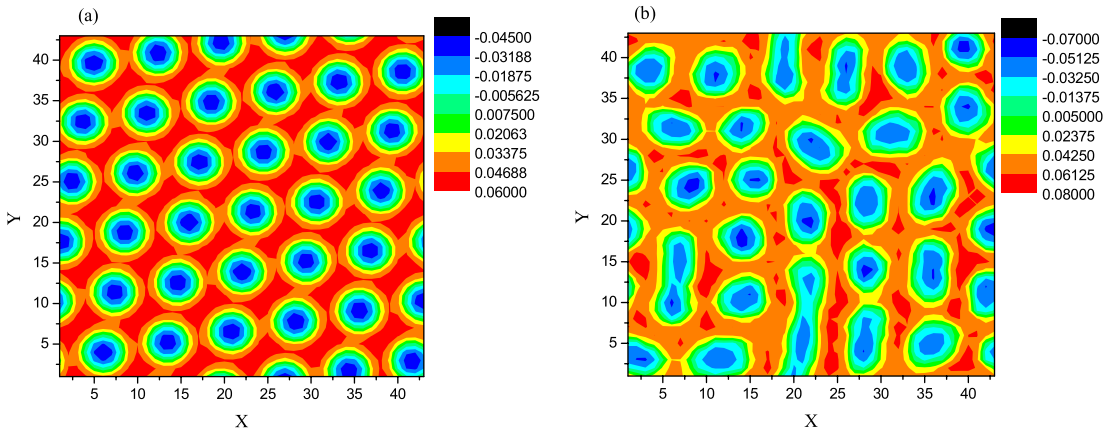

Figure 3. The out-of-plane polarization of (a) [100] ordered and (b) disordered PZT films under the global field of $E = 23 \times 10^7$ V m^{-1}. The size of the supercell is $43 \times 43 \times 4$.

for the [100] order PZT film. All of the nanodomains have almost the same circle shape. The distribution of nanodomain exhibits a good long-range order. However, if Zr and Ti are composition disordered, the ordered distribution of nanodomains is destroyed and the nanodomains also have different shapes (as shown in figure 3(b)). Some nanodomains are obviously longer in one direction than in another direction and can be regarded as nanobubbles [32].

The formation of the close packed arrangement of nanodomains results from the characteristic that stripes tend to have fixed width, which demands that the distance of between nanodomains is about an integer multiple of the stripe period. The close packed arrangement of nanodomains just meets the above demand. The nanodomain lattice constant is approximately equal to the stripe period, which is determined by the film thickness. With the increase of the electric field, the nanodomain lattice constant does not vary, but the diameter of the nanodomain will decrease. The same phenomena (i.e., two transformations of domain structure under the field) appear up to the thickest film (with a thickness of ten unit cells) that we simulate. The characteristic sizes of the domain structure such as the stripe width and the size of the nanodomains are determined by the film thickness. Therefore we can conveniently control the diameter of the nanodomain and the nanodomain lattice constant by choosing the film thickness and adjusting the field, which would be very useful in many respects such as as regards nonlinear photonic crystal [7] and the assembly of nanostructure [8, 9]. Due to the development of modern material processing technology, it is possible to prepare all kinds of PZT ultrathin films from disorder to complete [100] order. Since the distribution of nanodomains is strongly influenced by the ordering of the Zr and Ti in the atomic configuration, one may easily utilize the disorder effect in the nonlinear photonic crystal and the assembled nanostructure.

Two competing factors determine the above transformations. One is that the stripe width in ultrathin films is quite rigid and hardly changes with the varying external field. Another is that the field tends to induce as much parallel polarization as possible. The stripes antiparallel to the field have almost the same polarization as the stripes parallel to the field, indicating that ferroelectric off-centre displacement has a vortex structure [28]. Therefore, a parameter, λ, is introduced to reflect the ability of the domain structure to keep the polarization parallel to the field:

$$\lambda = \frac{A_+ - A_-}{A_+ + A_-} \tag{1}$$

where A_+ and A_- are respectively the areas of the domain in the field region with the polarization parallel and antiparallel to the field. The larger λ is, the higher the ratio of parallel polarization in the field region is, and the more energetically favourable the structure is under the field. When the stripe width is fixed, λ is equal to zero for the straight stripe patterns; and

$$\lambda = \begin{cases} \dfrac{4n-1}{4n^2-4n+1}, & \text{if } n \text{ is even,} \\ \dfrac{4n-3}{4n^2-4n+1}, & \text{if } n \text{ is odd,} \end{cases} \tag{2}$$

for the concentric loop stripe patterns, where n is the number of stripes. For example, we have $\lambda = 19/45$ when $n = 4$. And λ for concentric loop stripe patterns decreases with increasing n. The patterns with concentric loop stripes have larger λ than those with the straight stripes, and thus can be more stable under the external field. λ for the nanodomain structure (depicted in figure 2(b)) is larger than 0.5, which is far larger than that of any pattern with concentric loop stripes. However, in comparison with the concentric loop stripes case, the nanodomain lattice will have a larger residue depolarization field, corresponding to higher depolarization energy. This explains why the concentric loop stripe pattern is more stable under low field. However, the nanodomain lattice becomes more favourable with increasing field strength since it has large λ.

The incorporation of a ferroelectric into heterostructures with other functional materials can produce high electric field in the second component. The ferroelectric field effect has been demonstrated in many experiments [33–36]. The domain structures observed in this work are promising for producing an unusual field configuration with periodic direction change, which might result in some novel heterostructural effects. For example, the loop field configuration could be used to form a loop quantum well in the second component. Furthermore, the well width can be adjusted by changing the film thickness since the stripe width increases with the film thickness. It is expected that our results will not only lead to more interest in the study of the fundamental properties of ferroelectric ultrathin films, but also stimulate experimental investigations of such interesting self-organizing nanodomains.

Acknowledgments

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