Surface and size effects of low-dimensional ferroelectrics via multiscale electromechanically coupled computational methods

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Summary Electromechanically coupled computational methods in three levels have been developed in a bottom-up way, to investigate the surface and size effects of low-dimensional ferroelectric materials. The first-principles method is employed to explore the surface effect on the behavior of the cross-sectional polarization field for $BaTiO_3$ nanowires. The distribution of axial polarization is found to be dependent on the compositions of surface atoms, which can be well understood by a proposed surface-layer model. A shell-model based molecular dynamics method is developed for nanoscale ferroelectrics, which is validated by first-principles calculations and furthermore utilized to investigate both the size and strain effects of $BaTiO_3$ nanowires. The simulations indicate that the strain and size effects play some equivalent roles on the ferroelectric properties. Furthermore, an unconventional phase field method is proposed to investigate the size dependence of domain configuration and evolution in ultrathin ferroelectric films.

FIRST-PRINCIPLES STUDY ON SURFACE EFFECT OF $BATIO_3$ NANOWIRES

The first-principles method is employed to explore the behavior of the cross-sectional polarization field for thin nanowires of barium titanate [1]. Four different surface atomic configurations (Figs. 1a-1d) are taken into account, and topological defects of different winding numbers have been obtained (Figs. 1e-1h), beyond the known textures in ferroelectric nanostructures. They result from the inward accommodation of the polarization patterns imposed at the surface of the wire by surface and edge effects. The axial polarization also distributes differently for different surface terminations (Figs. 1i-1l). Based on the first-principles and MD calculations on the inhomogeneous polarization distribution, a surface-layer model is established by treating the nanowire as a compound of three parts: edge cell, surface cell, and inner cell. This model well predicts the different polarization results for different surface structures, as predicted by the first-principles calculations. Furthermore, this model indicates that lattice mismatch mechanism plays a very important role in the polarization distributions.

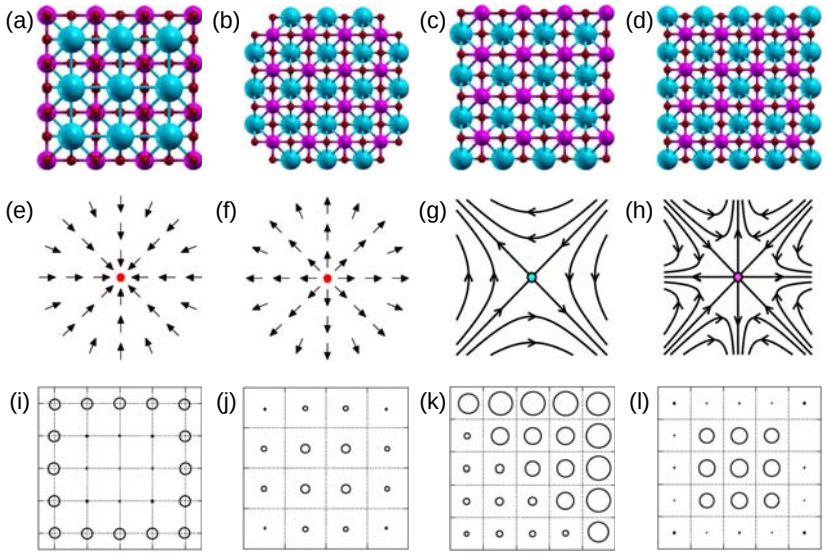

Fig. 1. Four different cross-sectional atomic configurations of $BaTiO_3$ nanowires (a-d), and the corresponding distributions of cross-sectional polarization components (e-h) and axial polarization components (i-l) [1]. In (a)-(d), the largest, moderate and smallest atoms in the figure denote Ba, Ti and O, respectively. In (e)-(h), the arrow represents the polarization component along the cross-section. In (i)-(l), the area of the circle denotes the magnitude of axial polarization.

MOLECULAR DYNAMICS STUDY ON SIZE AND STRAIN EFFECTS OF $BATIO_3$ NANOWIRES

To study a large atomic system, a shell-model based molecular dynamics method is developed for nanoscale ferroelectrics [2], which is validated by first-principles calculations on the structural parameters and polarizations of bulk material and nanowires. This method is utilized to investigate the size effect and strain effect of $BaTiO_3$ nanowires. Unusual stepwise hysteresis loops, and core-shell polarization structures with opposite polarization directions at the outer and inner regions of the nanowire are revealed in our simulations (Fig. 2). Moreover, the strain effect and size effect are found to play some equivalent roles on the ferroelectric properties of $BaTiO_3$ nanowires.

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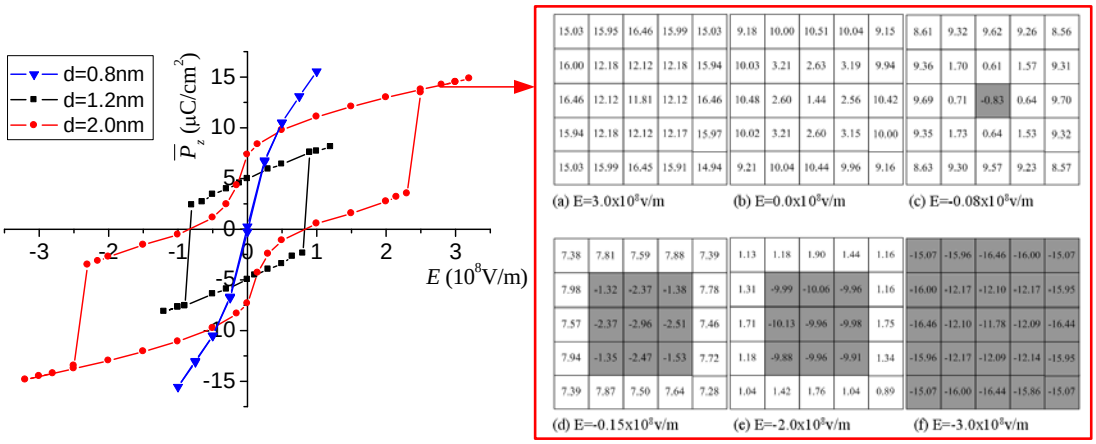

Fig. 2. The size dependent hysteresis loops of TiO_2 teminated $BaTiO_3$ nanowires and the corresponding domain evolutions for 2.0nm thick nanowire under an alternating electric field [2]. Each square in the right figure represent a lattice cell, and the number in the square denotes the axial polarization value.

PHASE FIELD INVESTIGATION ON SIZE DEPENDENT DOMAIN CONFIGURATION IN ULTRATHIN FERROELECTRIC FILMS

An unconventional phase field method is proposed to investigate the size dependence of domain configuration and evolution in ultrathin ferroelectric films [3]. The predicted domain structures agree with the MD simulations and experiments for ultra-thin films (e.g. thickness h<4.8nm) and relative thick film (e.g. h>20nm). Furthermore, the simulations reveal that four types of compatible domain structures exist at different thicknesses, with the number of coexisting variants decreasing with the film thickness.

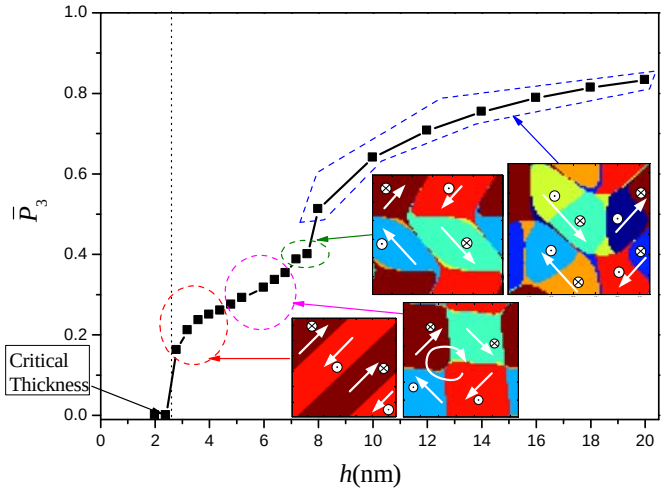

Fig. 3. The size dependent out-of-plane polarization and domain pattern [3]. The domain exhibits a zigzag pattern with 8 variants coexisting when h>7.6nm, a zigzag pattern with 4 variants coexistence when 6.8nm<h<8.0nm, a vortex pattern with 4 variants coexisting when 4.4nm<h<7.2nm, and a stripe pattern with 2 variants coexisting when 2.4nm<h<4.8nm; when the thickness is smaller than 2.8nm, the domain disappears, indicating that the ferroelectricity is suppressed.

CONCLUSIONS

Multiscale electromechanically coupled computational methods have been developed in a bottom-up way, to investigate the surface and size effects of low-dimensional ferroelectric materials. Several physical phenomena and underlying mechanisms are revealed, which can help understand the ferroelectric properties of low-dimensional ferroelectrics.

References

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