A PHASE FIELD STUDY ON THE DOMAIN PATTERNS AND HYSTERESIS LOOPS OF FREE-STANDING FERROELECTRIC NANO-THIN FILMS

Yu Su* & George J. Weng**a)
*Department of Mechanics, School of Aerospace Engineering, Beijing Institute of Technology, Beijing, 100081, China
**Department of Mechanical and Aerospace Engineering, Rutgers University, New Brunswick, NJ 08903, USA

Summary Surface tension induced by nanoscale ferroelectric thin films can have significant effects on domain patterns and hysteresis behavior. To uncover these effects, a 2-D phase field model is developed for $BaTiO_3$ nano-thin films. It is demonstrated that there always exists a thin layer of domains near the surface due to surface tension. Both remnant polarization and coercive field are found to decrease with the increase of surface tension and decrease of film thickness, which could eventually result in a loss of ferroelectricity.

INTRODUCTION

Thickness dependence of ferroelectric properties for nanoscale ferroelectric thin films has been widely reported in recent literatures. In thin film-substrate systems such size dependence can be affected by several factors such as depolarization field, interface effect, and lattice mismatch strain. In addition, it is well known that nanoscale materials possess higher energy at the free surfaces leading to surface tension. This intrinsic surface stress along the free surfaces can also cause considerable size dependence for ferroelectric properties. In order to provide better understanding on the effect of surface tension, we will consider the behavior of free-standing nano-thin films. Study of a free-standing nano-thin film allows us to isolate the effect of surface tension from other factors and it could bring new insights into its size-dependent properties. To this end we will invoke a phase-field model to examine the domain patterns and hysteresis loops of the nano-thin films as a function of film thickness and surface tension.

THE THERMODYNAMICS-BASED CONTINUUM PHASE FIELD MODEL

In this phase field model the Helmholtz free energy of the system is set to depend on strain, electric displacement, an order parameter and its gradient, i.e., $\Psi(\varepsilon_{ij},D_i,P_i,P_{i,j})$, where ε_{ij} is strain and D_i the electric displacement. The electrical polarization P_i is taken as the order parameter and the subscript ", j" represents partial differentiation with respect to the x_j coordinate direction. The work-conjugates of these parameters are stress, electric field, and micro-forces, respectively. The governing equation that describes the temporal evolution of the spontaneous order parameters can be written as [1]

$$\left(\frac{\partial\psi}{\partial P_{i,j}}\right)_{,j} - \frac{\partial\psi}{\partial P_i} + \gamma_i = \beta_{ij}\left(\frac{\partial P_j}{\partial t}\right) \quad . \tag{1}$$

Eq. (1) is essentially a generalized form of Ginzburg-Landau equation, where γ_i represents the external micro-force, β_{ij} the inverse mobility tensor, and t the time. A general form of the free energy is

$$\begin{aligned}\psi = {} & \frac{1}{2}a_{ijkl}P_{i,j}P_{k,l} + \Big\{\frac{1}{2}\bar{a}_{ij}P_iP_j + \frac{1}{4}\bar{\bar{a}}_{ijkl}P_iP_jP_kP_l \\ & + \frac{1}{6}\bar{\bar{\bar{a}}}_{ijklmn}P_iP_jP_kP_lP_mP_n + \frac{1}{6}\bar{\bar{\bar{\bar{a}}}}_{ijklmnrs}P_iP_jP_kP_lP_mP_nP_rP_s\Big\} \\ & + \Big\{b_{ijkl}\varepsilon_{ij}P_kP_l + \frac{1}{2}c_{ijkl}\varepsilon_{ij}\varepsilon_{kl} + f_{ijklmn}\varepsilon_{ij}\varepsilon_{kl}P_mP_n \\ & + g_{ijklmn}\varepsilon_{ij}P_kP_lP_mP_n\Big\} + \frac{1}{2\kappa_0}\left(D_i - P_i\right)\left(D_i - P_i\right)\end{aligned} \tag{2}$$

where κ_0 is the permittivity of free space. In this work a principle of virtual work is specified for the theory and is implemented to devise a finite element formulation. The effects of surface tension for the nano-thin films can then be investigated with the phase field approach.

a) Corresponding author. Email: weng@jove.rutgers.edu

RESULTS AND DISCUSSION

A free standing thin film can be treated as a two-dimensional (2D) problem with free boundaries on both top and bottom surfaces subjected to tensile stresses or surface tensile strain, as shown in Fig. 1. The considered ferroelectric material is $BaTiO_3$ and the material properties are adopted from [1]. The length *l* of the periodic unit is set to be 800nm, and the total thickness *h* of the film is subject to change from several to tens of nanometers. The thickness of the pre-tensioned top region is fixed at h_s=1nm, regardless of the film thickness. The computation starts with an initial condition at which the spontaneous polarizations form 180° stripe domain structures [2,3]. The total number of time steps for each increment of electric field is set to be large enough so that the system can reach full equilibrium state.

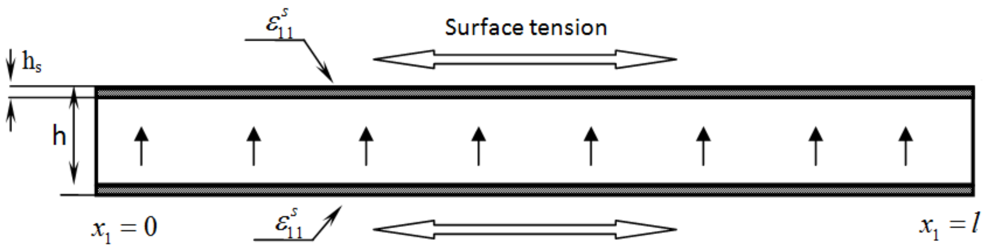

Fig. 1 The geometric model of a free-standing $BaTiO_3$ nano-thin film.

The calculated effects on the hysteresis loops are shown in Fig. 2, with the film thickness of 20nm and 10nm, and surface tensile strain of 0, $0.5\varepsilon_0$, and $1.0\varepsilon_0$, where ε_0=0.82% is the spontaneous strain along the c-axis. It is evident that, within this range of surface tension, both remnant polarization and coercive field tend to decrease with increasing surface tension or decreasing film thickness. The evolution of domain patterns as the electric field increases is shown in Fig. 3 for the 20nm-thick film with prescribed strain of $0.5\varepsilon_0$. It can be seen that the initial symmetric stripe domain pattern as shown in the top figure (a) gradually turns into an asymmetric one as shown in middle (b), and eventually becomes a mono-domain in the interior of the nano-thin film. But in all cases it is also evident that there exists a thin domain layer near the free surface of the film, with its polarization direction strongly governed by the surface tension.

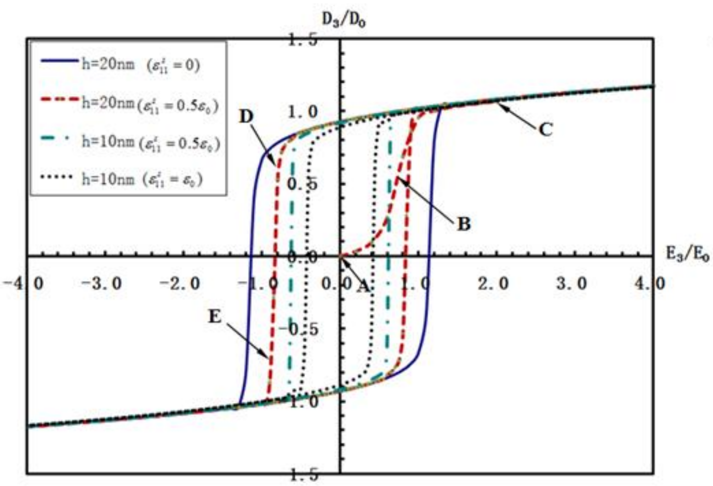

Fig. 2 The influence of surface tension and film thickness on the hysteresis loops.

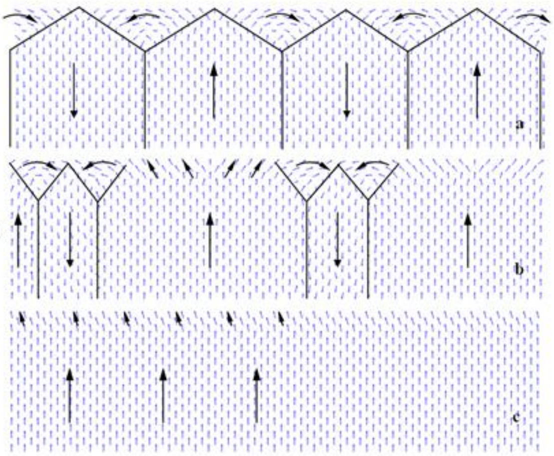

Fig. 3 Evolution of ferroelectric domains under increasing applied electric field.

Acknowledgements: Y. Su thanks the support of National Natural Science Foundation of China under Grants 11002024 and 11132011, and G.J. Weng thanks the support of the University of Hong Kong under the Visiting Research Professor Scheme 2010-2013 and Qatar National Research Fund NPRP 09-508-2-192.

References

[1] Su Y., Landis C.M.: Continuum thermodynamics of ferroelectric domain evolution: theory, finite element implementation, and application to domain wall pinning. *J. Mech. Phys. Solids* **55**: 280-305, 2007.

[2] Hong L., Soh A.K., Song Y., and Lim L.C.: Interface and surface effects on ferroelectric nano-thin films. *Acta mater.* **56**: 22966-2974, 2008.

[3] Weng G.J., and Wong D.T.: Thermodynamic driving force in ferroelectric crystals with a rank-2 laminated domain pattern, and a study of enhanced electrostriction. *J. Mech. Phys. Solids* **57:** 571-597, 2009.