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Citation: Applied Physics Letters 91, 112914 (2007); doi: 10.1063/1.2785121
View online: http://dx.doi.org/10.1063/1.2785121
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Prediction of ferroelectricity in BaTiO$_3$/SrTiO$_3$ superlattices with domains

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(Received 25 May 2007; accepted 27 August 2007; published online 14 September 2007)

The phase transitions of superlattices into single- and multidomain states were studied using a mesoscale phase-field model incorporating structural inhomogeneity, micromechanics, and electrostatics. While predictions of transition temperatures of BaTiO$_3$/SrTiO$_3$ superlattices into multidomains show remarkably good, quantitative agreement with ultraviolet Raman spectroscopic and variable-temperature x-ray diffraction measurements, the single-domain assumption breaks down for superlattices in which the nonferroelectric layer thickness exceeds the characteristic domain size in the ferroelectric layers. © 2007 American Institute of Physics. [DOI: 10.1063/1.2785121]

Superlattices represent a fascinating class of artificially grown thin films whose atomic structures can be precisely controlled using an epitaxial technique. Studies of ferroelectric/paraelectric superlattices such as KNbO$_3$/ KTaO$_3$, PbTiO$_3$/SrTiO$_3$, and BaTiO$_3$/SrTiO$_3$ (Refs. 5–12) have revealed that the transition temperatures ($T_c$'s) and ferroelectricity of a superlattice are strongly correlated to its structural periodicity, electrostatic interactions, and substrate strain. It has also been shown that interface contributions and the domain formation may affect the dependence of transition temperatures on superlattice structural periodicity. However, prior theories and atomistic calculations of superlattices have often been limited to transitions of a paraelectric superlattice to single domains within each layer of a superlattice or to a specific regular two-dimensional domain structure. In this letter, we present a theoretical model that incorporates the elastic interactions, substrate strain, electrostatic interactions, as well as three-dimensional multidomains without assuming the domain morphologies a priori.

As an example, we consider (BaTiO$_3$)$_n$/ (SrTiO$_3$)$_m$ superlattices, where $n$ and $m$ represent the number of perovskite unit cells along the growth direction of ferroelectric (001)$_n$ oriented BaTiO$_3$ (BT) and nonferroelectric (001)$_m$ oriented SrTiO$_3$ (ST), respectively, where the subscript $p$ denotes the pseudocubic unit cell. Our theoretical description is based on the phase-field method coupled with microelasticity and electrostatics. Despite its continuum nature, such an approach has been shown to provide accurate predictions of the strain effect on $T_c$ and domain structures of ferroelectric thin films. In this approach, the ferroelectric domain structure is described by the polarization distribution $\mathbf{P}(\mathbf{x}) = [P_1(\mathbf{x}), P_2(\mathbf{x}), P_3(\mathbf{x})]$, where $\mathbf{x} = (x_1, x_2, x_3)$.

The total free energy of a superlattice includes the bulk free energy, elastic energy, electrostatic energy, as well as the gradient energy, i.e., $F = \int V f_\text{bulk}(\mathbf{P}) + f_\text{elast}(\mathbf{P}, \mathbf{e}) + f_\text{elec}(\mathbf{P}, \mathbf{E}) + f_\text{grad}(\mathbf{P}_i, \mathbf{E}_j) dV$, where $V$ is the volume of the superlattice film and $\mathbf{P}_i = \partial \mathbf{P}_i / \partial x_i$. The polarization distribution for a given temperature and time is then obtained by
solving the time-dependent Ginzburg-Landau (TDGL) equations,

$$\frac{\partial P_i(x,t)}{\partial t} = -L \frac{\delta F}{\delta P_i(x,t)} \quad (i = 1,2,3),$$

(1)

where $L$ is the kinetic coefficient related to the domain wall mobility.

Figure 1(a) shows a schematic epitaxial superlattice consisting of periodically alternating (001)$_p$ ST and (001)$_p$ BT layers commensurately strained to the underlying (001)$_p$ ST substrate. As the film thickness of a superlattice is typically on the order of hundreds of nanometers or less, i.e., very thin substrate. The film thickness of a superlattice is typically commensurate to the underlying linear elasticity.

Figure 1(b) shows a schematic epitaxial superlattice consisting of periodically alternating (001)$_p$ ST and (001)$_p$ BT layers commensurately strained to the underlying (001)$_p$ ST substrate. As the film thickness of a superlattice is typically commensurate to the underlying linear elasticity.

We employed a simulation cell of $(64\Delta x_1)(64\Delta x_2) \times (N \Delta x_3)$, where $N=2(m+n)$ for a BT$_m$/ST$_n$ superlattice. A grid spacing of $\Delta x_1=\Delta x_2=1.0$ nm and $\Delta x_3=0.5\alpha_{ST}$ was used. The gradient energy coefficient was assumed to be isotropic with the nonzero independent one $g_{1111}=2.0$. $g_0$ is related to $\Delta x_1$ by $\Delta x_1=g_0/\alpha_0$ and $\alpha_0=[\alpha_{BT}]T=298$ K. The width of the BT/ST interface is assumed to be one grid spacing $\Delta x_3$.

Starting from a small random polarization distribution, we solved the coupled elastic, electrostatic, and the TDGL equations to obtain the domain morphologies. We identify the temperature below which there exists a spontaneous polarization as $T_c$.

Figure 2 summarizes the predicted $T_c$ as a function of BT and ST layer thicknesses for phase transitions into either a single domain (labeled 1D) with $P=P(x_3)$ or multidomain (labeled 3D) state with $P=P(x_1,x_3,x_3)$ as well as $T_c$ values determined from UV Raman and variable-temperature x-ray diffraction (VTXRD) measurements. As expected, $T_c$ increases with the number of unit cells $n$ of ferroelectric BT layers and decreases with the number of nonferroelectric ST unit cells $m$. While the difference in $T_c$ between transitions to single-domain and multidomain states is small for ST layer thickness $m=4$, for larger $m=13$ and $m=30$, the predicted $T_c$’s for transitions to single-domain states are significantly lower than those to multidomain states. Furthermore, based on the multidomain results, superlattices with $m=13$ and 30 have very similar $T_c$ values, implying that $T_c$ no longer changes with $m$ for large $m$, and the effect of the ST layer thickness on $T_c$ diminishes as the thickness of the BT layer $n$ increases. Finally, the predicted $T_c$’s for transitions to multidomain states and experimentally measured values show very good quantitative agreement.

To understand the difference between transitions to single-domain and multidomain states, we examined the polarization distribution and domain morphologies. An example of a domain morphology from a 3D simulation is shown in Fig. 3(a) for a BT$_8$/ST$_{13}$ superlattice at a tempera-
This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: superlattices.6 Our simulations show that the polarization in the ST layer is much smaller than the characteristic domain size within the ferroelectric layer, which are on the order of a couple of nanometers (∼3–4 nm in our particular example of BT$_n$/ST$_m$ superlattices).

In summary, we developed a phase-field model for predicting the phase transitions and ferroelectricity of superlattices. In particular, we studied the roles of multidomain states in phase transitions of superlattices. The predicted $T_s$ of ST/BT superlattices to multidomain states are in excellent agreement with experimental measurements, while the single-domain assumption breaks down at large thickness of the nonferroelectric layer, revealing the importance of domain formation in determining phase transition temperatures and other important aspects of ferroelectricity in superlattices.

This work was partially supported by Los Alamos National Laboratory Directed Research and Development Project under the United States Department of Energy (DOE), by NSF under DMR-0213623, DMR-0507146, and ECS-0210449, and by DOE under DE-FG02-01ER45907.

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19. BT$_n$/ST$_m$ superlattices. Our simulations show that the polarization in the ST layer disappears when the dipole-dipole interaction is artificially switched off. Therefore, the polarization within the ST is not the result of a ferroelectric phase transition, rather it is induced by the dipolar field produced by the BT layer, i.e., a result of a “ferroelectric proximity” effect. The induced polarization in the ST layer and thus the depolarization field can be significantly reduced or almost eliminated by the formation of domains within the BT layers. On the other hand, our simulations demonstrated that the effect of domains on $T_s$ can be neglected only if the thickness of the nonferroelectric layer is much smaller than the characteristic domain size within the ferroelectric layer, which are on the order of a couple of nanometers (∼3–4 nm in our particular example of BT$_n$/ST$_m$ superlattices).