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著者	川添　良幸
journal or publication title	APPLIED PHYSICS LETTERS
volume	93
number	24
page range	242905-1-242905-3
year	2008
URL	http://hdl.handle.net/10097/47085

doi: 10.1063/1.3040326

APPLIED PHYSICS LETTERS **93**, 242905 (2008)

Polarization switching in epitaxial films of $BaTiO_3$: A molecular dynamics study

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(Received 31 May 2008; accepted 12 November 2008; published online 18 December 2008)

We use molecular dynamics simulations with a first-principles model Hamiltonian to study polarization switching in ultrathin epitaxial films of $BaTiO_3$ sandwiched by ideal electrodes as a function of temperature and epitaxial strain. We find that the coercive fields of polarization switching reduce with tensile epitaxial strain and as temperature increases up to the transition, and depend sensitively on the nature of the epitaxial constraint. Our results should be directly relevant to the design of high frequency ferroelectric random access memories made with ultrathin epitaxial ferroelectric films. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3040326]

Ferroelectric (FE) materials are spontaneously polarized below a critical temperature and also have the ability to switch their polarization between two symmetry equivalent directions with external electric fields. As they maintain the polarized state even when the electric field is switched off,[1,2] they are technologically useful in nonvolatile memory devices.[3,4] With sustenance of ferroelectricity in ultrathin films[5,6] and recent advances in experimental techniques, it has become possible to grow high quality FE thin films on semiconductor[7] as well as metallic substrates,[8] opening up newer possibilities of use of FE thin films in nonvolatile ferroelectric random access memories (FERAMs).[3,9]

The FE properties of thin films are greatly influenced by epitaxial strain;[5] for example, epitaxial strain increases the values of remnant polarization P_r (compared to bulk) of 200 nm $BaTiO_3$ thin film grown on $GdScO_3$ and $DyScO_3$ substrates.[10] When the fluctuations in the in-plane strain of the film are suppressed (the strain is clamped) by a contact with the substrate, the film is termed as coherent with the substrate.[10] If the in-plane strains are free to fluctuate while maintaining the epitaxial strain constraint imposed through an epitaxial stress, it is termed as a partially relaxed film (RF). It was found experimentally by Choi *et al.*[10] that partially RFs of $BaTiO_3$ switch at lower coercive fields compared to the coherent ones. Magnitudes of coercive fields are found to increase with compressive in-plane strain for $Pb(Zr_{0.50}Ti_{0.50})O_3$ films.[11]

For technological applications, the FE thin films should have large P_r and small E_c (switching or coercive field). These properties relevant to polarization switching have been found to be sensitive to the nature of epitaxial conditions[10] and details of FE substrate-electrode interface.[12] Understanding of these issues can be achieved with atomistic, particularly first-principles simulations.[13] For example, these were used in the determination of epitaxial strain-temperature (ϵ-T) phase diagrams,[14,15] which were also obtained from phenomenological Landau–Devonshire theory.[16] Here we study polarization switching at few interesting points in the ϵ-T phase diagram[15] of ultrathin $BaTiO_3$ film sandwiched between ideal electrodes in the limit of *vanishing depolarization fields*. We present simulations of field driven polarization switching in (i) epitaxial coherent as well as (ii) partially relaxed $BaTiO_3$ film with thickness of 1.6 nm. We obtain information about the behavior of remnant polarization P_r and coercive fields E_c as a function of (i) fully versus partially coherent epitaxial film (EF), (ii) epitaxial strain, and (iii) temperature.

To model a FE thin film sandwiched between electrodes, the latter is treated as perfect electrostatic mirrors[13,15] between which the film is placed, and such a configuration allows us to use periodic boundary conditions with a supercell doubled along the direction perpendicular to the film, half of which corresponds to the film and the other half corresponds to its image in the electrode. We use here a $16 \times 16 \times 8$ supercell, which corresponds to a film with thickness of four unit cells (1.6 nm) (we note that the ϵ-T diagram was found to be almost independent of the film thickness[17]). Also, to estimate the dependence of E_c on the film thickness, we perform simulations on 8 (3.2 nm) and 12 (4.7 nm) unit cell thick films as well. Effects of depolarization fields are not considered here, the presence of which would result in the formation of stable striped-domain phase,[6,15] switching in which is complicated occurring at larger magnitudes of electric fields as shown in Ref. 13.

We use the model Hamiltonian derived from Ref. 18 and add a term $-V(\mathbf{P} \cdot \mathbf{E})$ to simulate the effects of electric field. A detailed description of the model and code used in our simulations can be found in Refs. 13 and 19, and the code can be downloaded from http://loto.sourceforge.net/feram/. The temperature is increased or decreased in steps of ~ 30 K until the target temperature at which switching to be studied is reached. Then, the electric field is increased in steps of ~ 5 kV/cm until it reaches a maximum $E_{\max}$, from which it is decreased from zero to $-E_{\max}$, and then again increased to $E_{\max}$, thereby completing one hysteresis loop.[13] At each temperature, strain, and field, the system is thermalized for 40 000 steps and thermal averaging of properties is performed over 60 000 steps.

We have studied films of two kinds:[10] (a) fully coherent EFs (system EF) where the in-plane strain degrees of freedom (DOFs) are fixed and (b) RFs, where the in-plane strain DOFs are allowed to change but subject to an in-plane stress: σ_{xx} and σ_{yy}, each with magnitude of -1.276 GPa, which corresponds to a strain of -1.3%, as in experiments on par-

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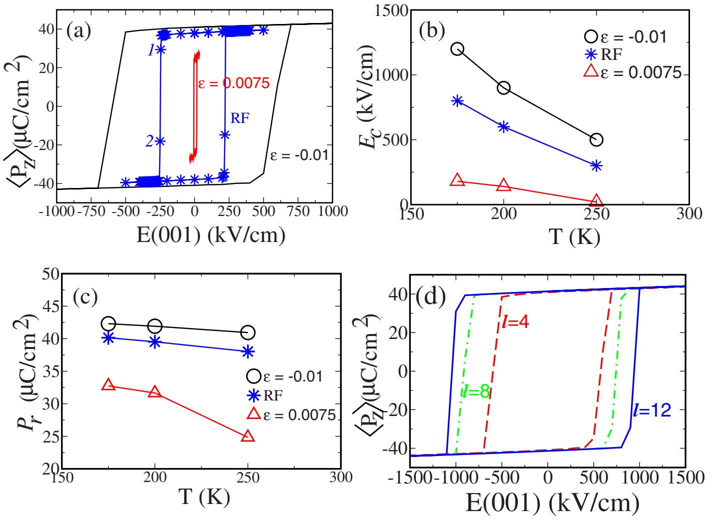

FIG. 1. (Color online) (a) Polarization (average) hysteresis at $T=250$ K for field applied along the (001) direction to EFs at $\epsilon=-0.01$ and $\epsilon=0.0075$ and RFs. Dependence of (b) E_c and (c) P_r on T in epitaxial and RFs. (d) Simulated polarization (average) hysteresis for compressively strained EFs ($\epsilon=-0.01$) with thicknesses of 4 (dashed line), 8 (dot-dashed line), and 12 (solid line) unit cells at 250 K.

tially relaxed BaTiO$_3$ on DyScO$_3$ substrate[10] (σ_{zz} is maintained at -5.0 GPa to compensate for the local density approximation errors in lattice constant[18]). System EF is simulated with two values of strain, -0.01 (compressive) and 0.0075 (tensile). Based on the ϵ-T phase diagram,[15] the former equals the strain of a coherent BaTiO$_3$ film grown on GdScO$_3$,[10] while the latter is a tensile strain close to the transition between tetragonal and paraelectric phases.[15] The latter was chosen to study the effects of the vicinity to a transition (as a function of temperature as well as strain) on switching. We have investigated polarization switching at three temperatures: 175, 200, and 250 K.

In experiments on single crystal of BaTiO$_3$, switching was observed to occur at ~ 1 kV/cm.[20] Our simulations with applied electric field along the (001) direction of the tetragonal bulk BaTiO$_3$ at 290 K exhibit switching at 60 kV/cm.[21] Thus the simulated switching field is an order of magnitude higher than its experimental value. This was also found in earlier[13,22] work and is mainly because switching in simulations is over short (less than nanosecond) time scales and suppresses formation of domains responsible for lower E_c. Our goal here is to study how single domain switching is different in bulk and in nanoscale EFs. We note however that our results are applicable for switching at high frequencies (>100 MHz). We find that coercive fields for epitaxial thin films [Figs. 1(a) and 1(b)] with ideal electrodes are (an order of magnitude) greater than those of bulk BaTiO$_3$ (similar to the experimental finding for piezoelectric transducer[23]).

Partial relaxation of films yields switching at lower E_c [Fig. 1(a)], consistent with experimental studies conducted on 200 nm BaTiO$_3$ film at 298 K.[10] Clamping the film to a substrate results in a coherent epitaxial strain throughout the film, forbidding relaxations in the in-plane strain DOFs. In contrast, for partially RFs, where the in-plane strain components are allowed to relax/fluctuate under the influence of an in-plane stress, any structural change would be facilitated by both in-plane and out-of-plane strain DOFs. As a result, the energy barrier for switching is reduced in the partially RFs, hence their lower coercive field.

Examination of the evolution of domains[24] during hysteresis of partially RF shows that domains of opposite polarization (Fig. 2) appear close to the coercive field, giving an overall polarization close to zero. For coherent EFs with compressive (tensile) strains, similar domains are observed, only at higher (lower) magnitudes of fields, compared to partially RFs. Switching facilitated by spontaneous nucleation of domains[25] is absent in all systems studied here since the time scale over which this occurs is much longer compared to the time scales of our simulations, and these simulations involve monodomain configurations as opposed to polydomain phases in experiments. We note that time in molecular dynamics simulations is real and our simulation duration is 0.2 ns.

We find that tensile epitaxial strain favors switching at much lower fields compared to relaxed or compressive EFs at any given temperature [Fig. 1(b)]. At $\epsilon=0.0075$ and $T=250$ K, switching occurs at a much lower $E_c=15$ kV/cm [Figs. 1(a) and 1(b)]. This can be understood with the concept of polarization rotation[26] that occurs through monoclinic (MC) phases. The film with a strain of $\epsilon=0.0075$ is in the region of the ϵ-T phase diagram (see Fig. 3 of Ref. 15) where (a) there is a crossover from one type of MC phase to another through a rhombohedral phase and (b) orthorhombic phase with in-plane polarization is readily accessible. As a result energy barriers for switching with rotation through these phases are expected to be very small and the switching occurs at low coercive fields. Interestingly, P_r is sizable at this temperature even if it is very close to the FE transition.

Irrespective of the nature of epitaxial strain, coercive fields decrease with increasing temperature as the system approaches a transition to paraelectric phase [see Fig. 1(b)]. This is because the energy barriers for switching, given by the free energy differences between different ordered and

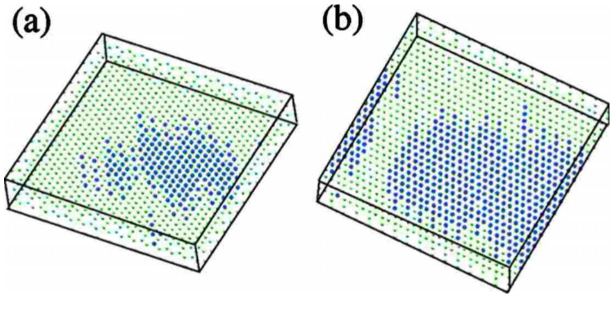

FIG. 2. (Color online) Polarization domains in the partially RF at 250 K at (a) $E=-245$ (001) kV/cm and (b) -250 (001) kV/cm [labeled as 1 and 2 in Fig. 1(a)]. Light green (light) and blue (dark) colors denote polarization along $+z$ and $-z$ directions, respectively.

cubic phases, reduce near the transition.[21] The remnant polarization P_r decreases slightly with increasing temperature for tensile strain and is almost independent of temperature for compressive strain [Fig. 1(c)]. While P_r is smaller by $\sim 10\ \mu\text{C/cm}^2$ in the tensile strained film than in the compressively strained EF, it is always greater than in the bulk ($26\ \mu\text{C/cm}^2$) (Ref. 20) at all temperatures.

While E_c is lower in partially RFs than in coherent EFs in our simulations, P_r is essentially the same in both (the difference is $\sim 2\ \mu\text{C/cm}^2$) [Fig. 1(c)]. On the other hand, P_r was found to be higher by $\sim 20\ \mu\text{C/cm}^2$ in partially RF than in the fully coherent 200 nm thick films of $BaTiO_3$ in experiment.[10] We believe that such behavior may be due to chemical details of the film-electrode interface ignored in the present simulations (note that the $GdScO_3$ and $DyScO_3$ substrates were used to grow coherent and partial RFs in experiments,[10] and ferroelectricity was shown to depend on details of the interface[12]).

Our simulations of thicker (3.2 and 4.7 nm) films with (i) compressive, (ii) tensile, and (iii) partially relaxed strains at 250 K show that coercive fields are higher compared to the film 1.6 nm thick [Fig. 1(d)] in variance with the Kay–Dunn law. This is because the Kay–Dunn law applies typically to films where the switching occurs through the inhomogeneous[27,28] nucleation of domains often pinned by the presence of defects.[13] The size and time scales of these phenomena are outside the scope of the present simulations.[13]

In summary, our findings that the coercive fields reduce with increasing temperature and upon partial relaxation of epitaxial FE films are consistent with experimental observations.[10] An important message is that the films grown with epitaxial strain on ideal electrodes close to the crossover between two MC phases in the ϵ-T phase diagram are predicted to have sizable polarization and fairly low switching fields necessary for FERAM applications. Present results are relevant to high frequency operations of FERAMs and longer simulations are necessary for applications at lower frequencies.

J.P. acknowledges CSIR (India) for a fellowship and we are grateful to the CCMS supercomputing facility at JNCASR.

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