Interface-Induced Polarization and Inhibition of Ferroelectricity in Epitaxial $SrTiO_3/Si$

A. M. Kolpak,[1,2] F. J. Walker,[1,2] J. W. Reiner,[1,2] Y. Segal,[1,2] D. Su,[3] M. S. Sawicki,[1,4] C. C. Broadbridge,[1,4] Z. Zhang,[5] Y. Zhu,[1,3] C. H. Ahn,[1,2] and S. Ismail-Beigi[1,2]

[1]*Center for Research on Interface Structures and Phenomena, Yale University, New Haven, Connecticut 06520-8284, USA*
[2]*Department of Applied Physics, Yale University, New Haven, Connecticut 06520-8284, USA*
[3]*Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973-5000, USA*
[4]*Department of Physics, Southern Connecticut State University, 501 Crescent Street, New Haven, Connecticut 06515, USA*
[5]*Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA*

(Received 19 June 2010; published 17 November 2010)

We use $SrTiO_3/Si$ as a model system to elucidate the effect of the interface on ferroelectric behavior in epitaxial oxide films on silicon. Using both first-principles computations and synchrotron x-ray diffraction measurements, we show that structurally imposed boundary conditions at the interface stabilize a fixed (pinned) polarization in the film but inhibit ferroelectric switching. We demonstrate that the interface chemistry responsible for these phenomena is general to epitaxial silicon-oxide interfaces, impacting on the design of silicon-based functional oxide devices.

DOI: 10.1103/PhysRevLett.105.217601 PACS numbers: 77.22.Ej, 68.37.Ma, 77.55.Px

The direct coupling of material properties across a nanoscale interface is a promising route to achieving new types of functionality unavailable in bulk materials. The successful epitaxial growth of perovskite oxides on silicon [1,2] is a promising avenue for realizing such coupling between ferroelectric and semiconducting layers. For example, high quality epitaxial $SrTiO_3$ thin films can be grown directly on silicon substrates. Furthermore, a room-temperature ferroelectric transition has been predicted for $SrTiO_3$ when strained to the Si lattice constant [3]. However, the presence and structure of the epitaxial interface can strongly influence the behavior of the adjacent materials relative to their bulk properties. The epitaxial $SrTiO_3/Si$ system is a useful model to study these interface effects in order to establish the degree to which the interface modifies or controls the behavior of such nanoscale oxide structures.

Because of strain relaxation [4], the possibility for strain-induced ferroelectric $SrTiO_3/Si$ is limited to very thin $SrTiO_3$ films. In such thin films, depolarizing fields reduce or eliminate polarization [5–7]. Interestingly, experiments indicate that ultrathin $SrTiO_3$ films on Si are nevertheless polar [4] and possibly ferroelectric [8], suggesting that interface and/or surface phenomena [9–12] play an important role in the system. While the atomic structure and electronic properties of the $SrTiO_3/Si$ interface are well studied [13–21], the relationship between the interface and the potential ferroelectric properties has not been examined. More generally, the effects of interface structure and chemistry on the properties of complex oxide films on semiconductors are unknown.

In the following, we apply both theory and experiment to demonstrate the crucial role of the interface in governing the properties of the $SrTiO_3/Si$ system. Using density functional theory (DFT), we show that the chemical interactions at the interface impose both mechanical and electrostatic boundary conditions on the oxide polarization, inducing a significant positive polarization in the oxide film despite large depolarizing field effects. Furthermore, we show that the interface interactions, which are general to Si-oxide interfaces, prevent ferroelectricity since they prevent the metastable interface structure associated with negative film polarization. Finally, we present synchrotron x-ray diffraction (XRD) data confirming our theoretical predictions of an interface-driven polarization and a lack of ferroelectricity in epitaxial $SrTiO_3/Si$.

To understand the role of the interface, we perform DFT calculations to determine the minimum energy atomic structures for 56 different $SrTiO_3/Si$ interface compositions with varying amounts of Sr, O, Ti, and Si in the interface region [22]. For each composition, we search for metastable states with positive, negative, and zero polarization [22]. We also determine the thermodynamic stability of the different $SrTiO_3/Si$ interface compositions, which includes all compositions and structures published to date [22]; under the experimentally verified constraints that neither SiO_2 nor $TiSi_2$ forms at the interface, we predict the most stable interface composition and geometry, illustrated in Fig. 1.

The predicted structure is in excellent agreement with scanning transmission electron microscopy (STEM) data, as shown by the superposition along both in-plane directions in Fig. 1. The structure also agrees with previous TEM studies [23] and synchrotron XRD measurements [22]. Furthermore, it is the only structure that matches four key observed STEM characteristics: (i) (1×1) in-plane symmetry, (ii) lack of Si dimers, (iii) a full monolayer of Sr at the interface, and (iv) alignment of the interfacial Si with the Ti-O columns. In the following, we focus on this structure as our primary example. We note that it is possible that differences in the growth may result in other interfacial structures, a number of which

 © 2010 The American Physical Society

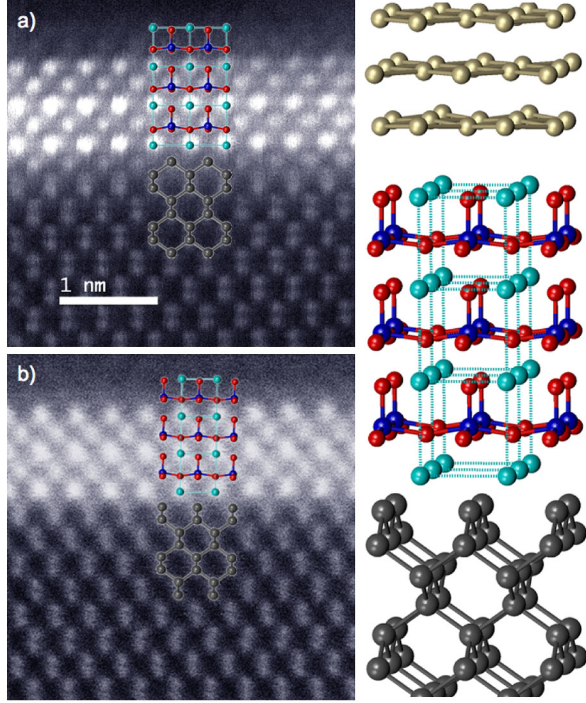

FIG. 1 (color online). STEM images of the $SrTiO_3/Si$ interface structure along the Si [110] (a) and [− 110] (b) directions. The overlaid DFT structures are uniformly scaled. (c) 3D view of the computed atomic structure of the predicted interface. Si, Sr, Ti, O, and Au are grey, cyan, blue, red, and gold, respectively.

TABLE I. DFT computed δz_{int} and δz_{avg} for $Au/SrTiO_3/Si$ films with different interface compositions; δz_{avg} values are for 3-unit-cell-thick films. Columns 1 and 2 show the composition of the atomic layer directly above the Si (the interface layer) and the oxide plane adjacent to the interface layer, respectively. The relaxed structures are shown in the supplement [22]. Because of the large interface effect, all thin films have a net positive polarization (positive δz_{avg}) despite depolarizing and thin film effects. For reference, the computed Berry phase polarization for bulk $SrTiO_3$ under 1.7% compressive strain is 0.35 C/m^2, and $\delta z_{bulk} = 0.17$ Å. ML = monolayer.

Interface layer	1st oxide layer	δz_{int} (Å)	δz_{avg} (Å)
1 ML Sr	1 ML TiO_2	0.35	0.29
1 ML Sr, 1 ML O	1 ML TiO_2	0.25	0.23
$\frac{1}{2}$ ML Sr	1 ML TiO_2	0.24	0.21
$\frac{1}{2}$ ML Sr, 1 ML O	1 ML TiO_2	0.10	0.09
$\frac{1}{2}$ ML Sr, $\frac{3}{2}$ ML O	1 ML TiO_2	0.10	0.09
1 ML Sr	1 ML SrO	0.47	0.24
1 ML Sr, 1 ML O	1 ML SrO	0.60	0.31
$\frac{1}{2}$ ML Sr	1 ML SrO	0.26	0.12
$\frac{1}{2}$ ML Sr, 1 ML O	1 ML SrO	0.18	0.05
$\frac{1}{2}$ ML Sr, $\frac{3}{2}$ ML O	1 ML SrO	0.15	0.04

have been previously proposed [13,14,16–20]; however, we show below that our main conclusions are insensitive to the details of the interface structure and can in fact be extended to epitaxial Si-oxide interfaces in general.

Our DFT calculations demonstrate that $SrTiO_3/Si$ has a net positive polarization in the $SrTiO_3$ film in each of the 56 interface compositions studied. (Positive polarization is directed away from the Si substrate.) The polarization in the oxide layer adjacent to the interface (characterized by the cation-oxygen displacement, δz_{int}) [24] is greater than or comparable to the polarization in bulk strained $SrTiO_3$ (δz_{bulk}), as Table I shows for representative interface compositions. Away from the interface, the polarization decreases, asymptoting to a finite positive value or zero, depending on the presence of external screening charges. The resulting net positive polarization, indicated by the average cation-oxygen displacement throughout the film, is given for films with a variety of interface compositions in Table I.

Figure 2(a) shows the energy versus δz_{int} for the predicted interface, demonstrating the stability of the positively poled ground state and the absence of a metastable negatively poled state. It is evident from the figure that the interface energetics completely dominate the system, overwhelming any tendency for ferroelectricity in the oxide film. This phenomenon is not unique to the predicted structure: we find no evidence for a metastable negatively poled state for *any* interface composition.

The absence of a metastable negatively poled state is largely due to the fact that δz_{int} is a fixed structural property of the interface. We demonstrate this point for the predicted structure by modifying the boundary conditions at the top oxide/electrode interface. Changing the electrode work function via different electrode materials modifies the screening charge, resulting in a change in the net polarization as illustrated in Fig. 2(b). However, the interface polarization (δz_{int}) remains constant regardless of the strength of the perturbation to the system. Even replacing the top electrode by a full monolayer of surface oxygen vacancies, which induces a large, monodomain negative polarization in thin film ferroelectrics [25], does not alter δz_{int}, despite inducing a small net negative film polarization. While of a different origin, the interface-dominated behavior illustrated in Fig. 2(b) is analogous to the surface/interface effects observed in several ferroelectric thin film systems [9–11,26].

The origin and universality of the observed boundary condition at the interface are both consequences of the interface chemistry, which leads to an electronic dipole across the interface for all compositions. (This interface electronic dipole is distinct from the interface polarization, which arises from ionic displacements in the $SrTiO_3$ layer, δz_{int}.) The dipole formation is driven by the interfacial O anions, which lower their (Madelung) potential energy by forming ionic bonds with the Sr cations in the interface buffer layer. As a result, the oxygens become more attractive to electrons, and the center of the electron distribution shifts closer to the first oxide plane. The redistribution of electrons from the hybrid Si/Sr states [27] (pink) into the lower energy O p-derived bonding states (blue) is apparent

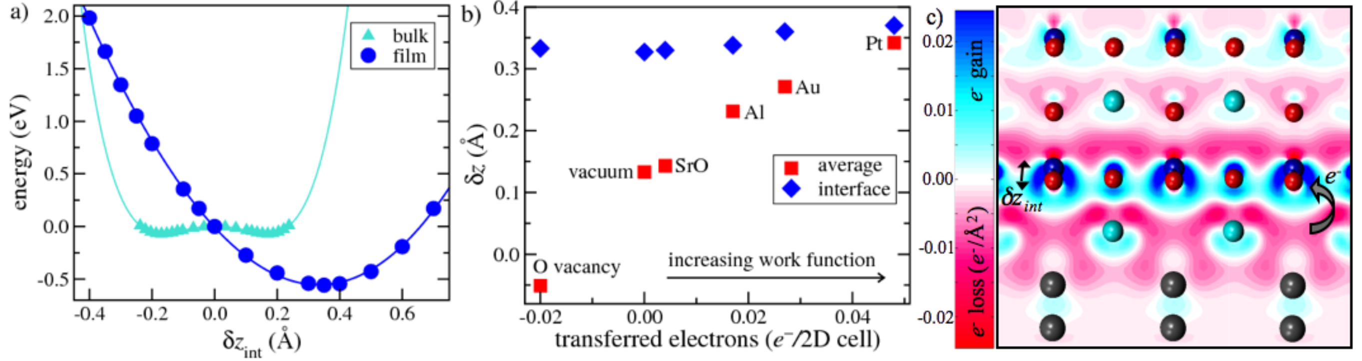

FIG. 2 (color online). (a) Computed energy versus $\delta z_{\rm int} = z_{\rm cation} - z_{\rm O}$ for a 3-unit-cell-thick film with the predicted interface composition (circles). The bulk polarization contribution (the energy of 3 unit cells of bulk strained $SrTiO_3$) is shown for comparison (triangles). (b) Average and interface δz for 3-unit-cell-thick films as a function of electrode material (indicated by labels next to each data point). (c) Computed electron rearrangement perpendicular to the interface due to interface formation. The arrow indicates the net shift of electron density from the Si/Sr region into the first oxide layer. Si, Sr, Ti, O, and Au atoms are grey, cyan, blue, red, and gold, respectively.

in Fig. 2(c), which shows the computed change in electron density due to interface formation for the predicted interface structure. The same phenomenon is observed for all interface compositions in our study; in fact, any atomically abrupt interface between Si and an oxide is expected to have a dipole in the *same* direction, as electrons will shift across the interface towards the oxygen, the most electronegative element in the system.

The large, positive values of $\delta z_{\rm int}$ reported in Table I arise directly from the interfacial electron rearrangement: the cations (anions) are repelled (attracted) by the positively charged Si/Sr interface region, driving them to displace away from (towards) the Si substrate. The interface displacement couples to the soft mode in the $SrTiO_3$ so that the interface polarization propagates into the film; a similar phenomenon is observed in the epitaxial BaO/Si interface system [28]. Aside from this mechanical coupling, the interface dipole creates a potential drop across the interface region that results in an electrical bias: the polarization profile in the $SrTiO_3$ film adjusts to compensate this voltage drop (a net positive polarization is needed). Hence, the chemically enforced electronic interface dipole creates both a mechanical and an electrical bias that work in tandem to ensure that the ground state is characterized by a net positive polarization in the $SrTiO_3$. This clarifies the difficulty of stabilizing a negative polarization: doing so requires formation of an interface dipole opposite to the intrinsic one and an interface structure in which oxygen acts as the electro-*positive* element—an unphysical possibility.

The interface features described above have important implications for the potential ferroelectric behavior of the $SrTiO_3$/Si system: By pinning the polarization, the interface prevents ferroelectric switching between monodomain polarization states. The single energy minimum nature of the interface also inhibits domain formation, which often occurs to alleviate depolarizing fields in thin ferroelectric films: as Fig. 2(a) shows, a negatively poled domain is mechanically unstable and has a prohibitive energy cost compared to the energy that can be gained by the ferroelectric distortion—i.e., there is no driving force for domain formation in the $SrTiO_3$/Si system [29].

The intrinsic, chemomechanical origin of the interface phenomena strongly suggests that the behavior of the $SrTiO_3$/Si system is generalizable to nonpolar oxide-semiconductor interfaces. Indeed, substituting the $SrTiO_3$ in our calculations with $PbTiO_3$ or $BaTiO_3$ results in a similar interfacial electron rearrangement and a large, positive $\delta z_{\rm int}$, demonstrating that our results can be extended to other systems. This generality has important consequences for device design, as the fundamental interface properties inhibit the desired functionality.

Because of its origin, the polarization in the $SrTiO_3$/Si system is not only unswitchable, but also temperature-independent (i.e., the system will not exhibit a ferroelectric phase transition). We confirm this prediction experimentally using temperature-dependent anomalous XRD measurements to determine the displacement of the Ti from centrosymmetry [30]. The data shown in Fig. 3 demonstrate a temperature-independent polarization directed away from the Si. In addition, both the direction and magnitude of the displacement are in good agreement with our DFT results (dashed lines): our first-principles and experimental results are quantitatively consistent in finding an unswitchable interface-stabilized polarization.

The microscopic description of the $SrTiO_3$/Si interface presented here leads to the conclusion that neither epitaxial $SrTiO_3$/Si nor other similar perovskite/Si thin films can exhibit strain-induced ferroelectricity. This conclusion is seemingly in contrast with the recent observation of piezoforce microscopy (PFM) contrast in $SrTiO_3$/Si structures [8], since PFM contrast is routinely observed in canonical ferroelectric films. However, careful examination of the PFM time dependence of $SrTiO_3$ films [31] finds a behavior unlike that of normal ferroelectric materials: instead of exhibiting the stable PFM signal seen for ferroelectric

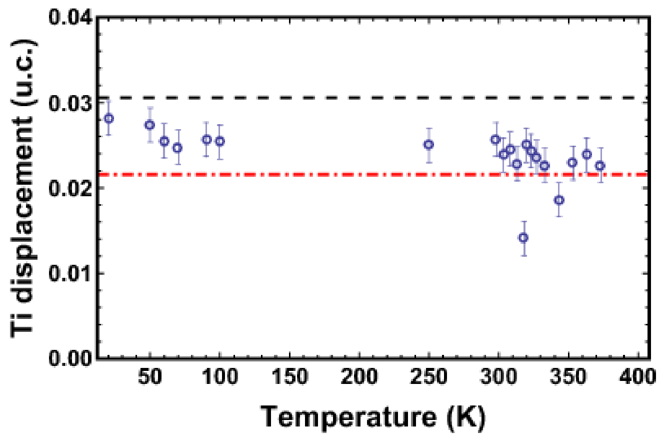

FIG. 3 (color online). Synchrotron XRD measurements of the Ti displacement versus T for a 5-unit-cell-thick $SrTiO_3/Si$ film. The blue dots are the experimental data; the black (red) dashed lines indicate the computed GGA (LDA) average displacement in films of the same thickness.

films, the signal from $SrTiO_3$ is found to decay. These results, which we have also confirmed on our samples, suggest that PFM measurements of $SrTiO_3$ are dominated by defect-related effects rather than intrinsic ferroelectric behavior. Further experiments, such as PFM measurements of epitaxial $BaTiO_3$ or $PbTiO_3$ thin films on Si, may help distinguish between strain- and defect-induced ferroelectricity, since these materials do not exhibit the type of defect-induced ferroelectricity that has been postulated in $SrTiO_3$ [12,31].

In summary, we demonstrate how interfacial chemistry and electrostatics create an interface-induced polarized ground state in ultrathin $SrTiO_3$ films grown epitaxially on Si, yielding a pedagogical example of how interfacial effects can dominate the behavior of nanoscale heterosystems and place limitations on direct coupling between the properties of functional oxides and semiconductors. Our conclusion that intrinsic $SrTiO_3/Si$ systems have a fixed polarization agrees with the existing experimental data, with significant implications for the design of oxide electronic devices: a strain mechanism alone will not provide the basis for novel ferroelectric behavior in this system. Looking forward, thoroughly understanding these interfacial effects is the first necessary step in designing new possibilities for chemical or mechanical modifications of the interface that allow direct coupling and lead to novel physics and interface-based functionalities.

We acknowledge support from the National Science Foundation under MRSEC DMR 0520495 and DMR 1006256, and SRC, as well as computational support from NCSA TeraGrid and Yale HPC. We thank the team of the 33ID beam line at the APS for technical assistance. Use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. Work at Brookhaven was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Science, under Contract No. DE-AC02-98CH10886.

[1] R. A. McKee, F. J. Walker, and M. F. Chisholm, Phys. Rev. Lett. **81**, 3014 (1998).
[2] J. W. Reiner *et al.*, Adv. Mater. **22**, 2919 (2010).
[3] J. H. Haeni *et al.*, Nature (London) **430**, 758 (2004).
[4] J. C. Woicik *et al.*, Phys. Rev. B **73**, 024112 (2006).
[5] J. W. Reiner *et al.*, Phys. Status Solidi B **241**, 2287 (2004).
[6] J. Junquera and P. Ghosez, Nature (London) **422**, 506 (2003).
[7] N. Sai and A. M. Kolpak, and A. M. Rappe, Phys. Rev. B **72**, 020101 (2005).
[8] M. P. Warusawithana *et al.*, Science **324**, 367 (2009).
[9] M. Stengel, D. Vanderbilt, and N. A. Spaldin, Nature Mater. **8**, 392 (2009).
[10] J. E. Spanier *et al.*, Nano Lett. **6**, 735 (2006).
[11] D. D. Fong *et al.*, Phys. Rev. Lett. **96**, 127601 (2006).
[12] M. Choi, F. Oba, and I. Tanaka, Phys. Rev. Lett. **103**, 185502 (2009).
[13] R. A. McKee *et al.*, Science **300**, 1726 (2003).
[14] C. J. Forst *et al.*, Nature (London) **427**, 53 (2004).
[15] A. A. Demkov *et al.*, Phys. Rev. B **71**, 195306 (2005).
[16] F. Niu and B. W. Wessels, J. Cryst. Growth **300**, 509 (2007).
[17] P. W. Peacock and J. Robertson, Appl. Phys. Lett. **83**, 5497 (2003).
[18] I. N. Yakovkin and M. Gutowski, Phys. Rev. B **70**, 165319 (2004).
[19] X. Zhang *et al.*, Phys. Rev. B **68**, 125323 (2003).
[20] L. F. Kourkoutis *et al.*, Phys. Rev. Lett. **100**, 036101 (2008).
[21] Y. Wang *et al.*, J. Phys. D **42**, 085409 (2009).
[22] See supplementary material at http://link.aps.org/supplemental/10.1103/PhysRevLett.105.217601.
[23] S. B. Mi *et al.*, Appl. Phys. Lett. **89**, 163507 (2006).
[24] The layer polarization can be approximated by $(\delta z/\delta z_{\mathrm{bulk}})P_{\mathrm{bulk}}$, where P_{bulk} and δz_{bulk} are the computed values for bulk $SrTiO_3$ under 1.7% compressive strain. This estimate does not account for possible inhomogeneity in the effective charges throughout the film, so we simply use δz to describe P in this work.
[25] R. V. Wang *et al.*, Phys. Rev. Lett. **102**, 047601 (2009).
[26] C. G. Duan *et al.*, Nano Lett. **6**, 483 (2006).
[27] K. Garrity and S. Ismail-Beigi, Phys. Rev. B **80**, 085306 (2009).
[28] Y. Segal *et al.*, Phys. Rev. Lett. **102**, 116101 (2009).
[29] Computations confirm the absence of stable multidomain structures (see supplement for details). In brief, without Si, thin $SrTiO_3$ films are weakly multidomain ferroelectric, but when the $SrTiO_3/Si$ interface forms, multidomain structures are highly unstable, relaxing to the monodomain, polar, nonferroelectric state (Fig. 1).
[30] S. J. van Reeuwijk *et al.*, J. Appl. Crystallogr. **37**, 193 (2004).
[31] H. W. Jang *et al.*, Phys. Rev. Lett. **104**, 197601 (2010).