Theory of hypothetical ferroelectric superlattices incorporating head-to-head and tail-to-tail 180° domain walls

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While electrical compatibility constraints normally prevent head-to-head (HH) and tail-to-tail (TT) domain walls from forming in ferroelectric materials, we propose that such domain walls could be stabilized by intentional growth of atomic layers in which the cations are substituted from a neighboring column of the periodic table. In particular, we carry out predictive first-principles calculations of superlattices in which Sc, Nb, or other substitutional layers are inserted periodically into $PbTiO_3$. We confirm that this gives rise to a domain structure with the longitudinal component of the polarization alternating from domain to domain, and with the substitutional layers serving as HH and TT domain walls. We also find that a substantial transverse component of the polarization can also be present.

In recent years, first-principles calculations have been used very successfully to explore superlattice structures based on ABO_3 perovskites and to predict their physical properties.[1–4] Because of the vast number of combinations that can be assembled from the elemental building blocks, first-principles calculations can provide a useful way to screen for desired physical properties and to study interesting possibilities theoretically before they are grown experimentally.[5,6] For example, Sai *et al.* predicted that a compositional perturbation that breaks inversion symmetry could increase the piezoelectric response,[1] and an enhancement of the spontaneous polarization in $BaTiO_3/SrTiO_3$ superlattices was predicted by Neaton *et al.* under certain conditions of epitaxial strain.[2] Also, the breaking of tetragonal symmetry has been predicted for certain $BaTiO_3/SrTiO_3$ superlattices,[3] and new phase diagrams have been predicted for superlattices composed of $Pb(Sc_{0.5+\mu}Nb_{0.5-\mu})O_3$ with certain layer sequences of composition μ.[4]

In the present work, we propose a new kind of superlattice structure which might be grown artificially via controlled layer-by-layer epitaxy techniques such as molecular-beam epitaxy[7] (MBE) or pulsed laser deposition (PLD).[8] These contain 180° ferroelectric domain walls, but of an unusual kind. Normally, 180° domain walls in a tetragonal ferroelectric such as $PbTiO_3$ form so as to obey electrical compatibility, leading to 180° domain walls running parallel to the tetragonal (polarization) axis. This occurs because a tilting of the 180° domain wall would lead to a polarization-induced bound charge on the domain wall, leading to a large and unfavorable electrostatic energy. Forcing the introduction of a "head-to-head" (HH) or a "tail-to-tail" (TT) domain wall perpendicular to the polarization direction would presumably cause it to become strongly metallic due to neutralization by free carriers.

However, we propose that intentional insertion of chemical substitutions in certain atomic layers during growth ("delta doping") could provide an approximate cancellation of this bound charge, allowing for the fabrication of new kinds of superlattice structures containing 180° HH and TT domain walls, as illustrated in Fig. 1. In this $PbTiO_3$ ex-

ample, the compensation is realized by substituting certain layers of Ti atoms by donor or acceptor atoms drawn from neighboring columns of the Periodic Table. If the substitutional charge density can be chosen to provide an approximate cancellation of the bound polarization charge of the HH or TT domain wall, then one may hope to arrive at a configuration that is both neutral and energetically favorable.

In this paper, we carry out first-principles density-functional calculations of superlattice structures such as the 8-cell one shown in Fig. 1 as a "proof of concept" for this idea. We find that this arrangement, with HH and TT domain walls at the acceptor and donor layers, respectively, is a robust configuration in which there is no gap closure (i.e., the superlattice remains insulating). Somewhat surprisingly, we also find that a small transverse component of the polarization develops, leading to an overall spontaneous polarization of the supercell in the [100] direction. This can be understood as arising from the imperfect compensation in this case.

We first select a host material for our superlattice, choosing a tetragonal material and letting its c axis be in the superlattice growth direction. In order to attain perfect compensation by a donor or acceptor layer of areal charge density $\pm e/a^2$, where a is the in-plane lattice constant, we would need a material whose spontaneous polarization P_s is $\pm e/2a^2$. Roughly, $a \simeq 4$ Å for most perovskites, in which case the matching condition is $P_s = 0.50$ C/m^2. Taking $KNbO_3$, $BaTiO_3$, and $PbTiO_3$ in their tetragonal phases,
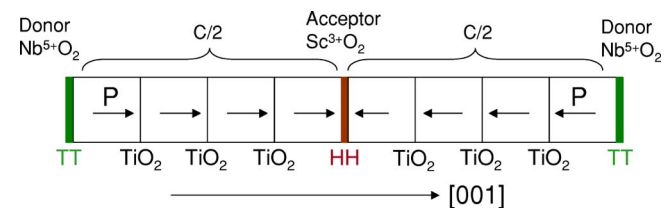

FIG. 1. (Color online) Sketch of $PbTiO_3$-based ferroelectric superlattice in which head-to-head and tail-to-tail 180° domain walls coincide with acceptor (Sc) and donor (Nb) substitutional layers, respectively.

these have P_s=0.40 C/m^2, 0.27 C/m^2, and 0.75 C/m^2, respectively. None of them is ideal, but we have chosen to carry out our pilot calculations here using PbTiO$_3$, whose polarization is somewhat larger than the nominal matching value. PbTiO$_3$ is a good test system, being a well-studied prototypical ferroelectric material having a simple phase behavior, remaining in the tetragonal ferroelectric phase from T=0 up to well above room temperature. Experimentally, alloy host materials such as Pb$_{1-x}$Sr$_x$TiO$_3$ or PbZr$_{1-x}$Ti$_x$O$_3$ might be used to tune the concentration to achieve more ideal matching of the polarization, but we have decided to limit ourselves to pure compounds for this first study.

We construct a 40-atom supercell by arranging 8 unit cells of bulk tetragonal PbTiO$_3$ in an $a \times a \times 8c$ supercell, with initial atomic coordinates chosen to be those of the relaxed bulk ferroelectric structure with polarization pointing in the [001] direction throughout the supercell. We then substitute the Ti atoms in the first TiO$_2$ layer by donor atoms, and the Ti atoms in the fifth TiO$_2$ layer by acceptor atoms, as shown in Fig. 1. We choose Nb (5+) as the donor and Sc (3+) as the acceptor because these atoms are commonly found on the B site of other perovskite ABO$_3$ oxides. We assume perfect control of the layer-by-layer composition, resulting in an ideal PbNbO$_3$/3 $\times$ PbTiO$_3$/PbScO$_3$/3 $\times$ PbTiO$_3$ structural sequence as shown Fig. 1.

We then relax the structure under a symmetry constraint that preserves the tetragonal $P4mm$ symmetry (i.e., atom displacements are allowed only in the z direction). The lattice constant is fixed in the in-plane directions, corresponding to conditions of epitaxial growth on a bulk tetragonal PbTiO$_3$ substrate. We also fixed the lattice constant along the [001] direction, assuming that the volume relaxations resulting from the compensation would be small. All calculations were performed at zero temperature.

The first-principles calculations were carried out using the Vienna *ab-initio* simulations package (VASP),[9] in which density-functional theory within the local-density approximation[10] is implemented. A plane-wave basis set and projector augmented-wave potentials[11] were used with a 400 eV energy cutoff for the electronic wave functions. Brillouin zone integrations were performed on a Monkhorst-Pack mesh of dimensions $4 \times 4 \times 2$ and $10 \times 10 \times 2$ for structural relaxation and density-of-states (DOS) calculations, respectively. The ionic relaxation was considered to be achieved when the Hellmann-Feynman forces on the ions were less than 3 meV/Å.

We find that the structural relaxation converges towards a structure in which the polarization reverses in the top half of the unit cell and the system acquires an M_z mirror symmetry across the planes containing the donor and acceptor atoms, converting these layers into 180° TT and HH domain walls as anticipated in Fig. 1. When we observed this apparent convergence towards the higher-symmetry $P4/mmm$ structure, we carried out the final relaxation with this $P4/mmm$ symmetry enforced, and confirmed that the resulting structure had a lower energy.

In order to test whether this $P4/mmm$ is really the structural ground state, we gave additional small displacements to the atoms in order to break the tetragonal symmetry and carried out further relaxations. Surprisingly, we found that
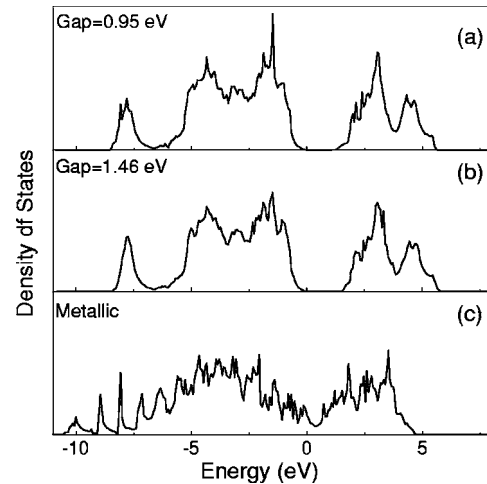

FIG. 2. Density of states (DOS) of 40-atom PbTiO$_3$ supercells considered in the text. (a) $P4/mmm$ supercell of Fig. 1 containing HH and TT domain walls compensated by impurity layers. (b) Same, but with in-plane component of polarization ($Pmm2$ symmetry). (c) Reference structure in which polarization reverses as in Fig. 1, but no compensating impurity layers are present.

the system is unstable to the growth of an in-plane component of the polarization. We tested both initial [100] displacements and initial [110] displacements (preserving, in both cases, the M_z symmetry), giving rise to $Pmm2$ and $Amm2$ structures, respectively. We find that the relaxed $Pmm2$ structure has an energy 0.065 eV lower than that of the $P4/mmm$ structure, while the relaxed $Amm2$ one is 0.057 eV lower than the $P4/mmm$. Thus, we find that the $Pmm2$ structure is our final structural ground state.

To get a better sense of the electronic structure of the relaxed structures, we computed the electronic density of states (DOS). The results, shown in Figs. 2(a) and 2(b) for the $P4/mmm$ and $Pmm2$ structures respectively, indicate that the compensation is successful and the entire superlattice is insulating. (The DOS for the $Amm2$ structure looks very similar to these.) The final gap of 1.46 eV is moderately smaller, but not drastically smaller, than the gap of 1.78 eV for bulk tetragonal PbTiO$_3$. (As these gaps are computed using the LDA, they should be regarded as underestimates of the true gaps.)

We also checked what happens if there is no compensation between the polarization-induced bound charge and the donor/acceptor layer. To do this, we constructed a 40-atom $P4/mmm$ supercell similar to that of Fig. 2(a), but without introducing the impurity layers. (Actually, this was done by imposing the displacement pattern of the ferroelectric tetragonal ground state of PbTiO$_3$, but with opposite signs in the bottom and top halves of the supercell.) The result is shown in Fig. 2(c), where it is clear that the structure is strongly metallic. Thus, the compensation by the donor and acceptor layers is essential in order to arrive at an overall insulating structure.

We return now to the pattern of ground-state atomic displacements that we calculated for the $P4/mmm$ and $P2mm$ structures of Figs. 2(a) and 2(b), and interpret these in terms of a local polarization in each unit cell. To do this, we model the local polarization as[12]
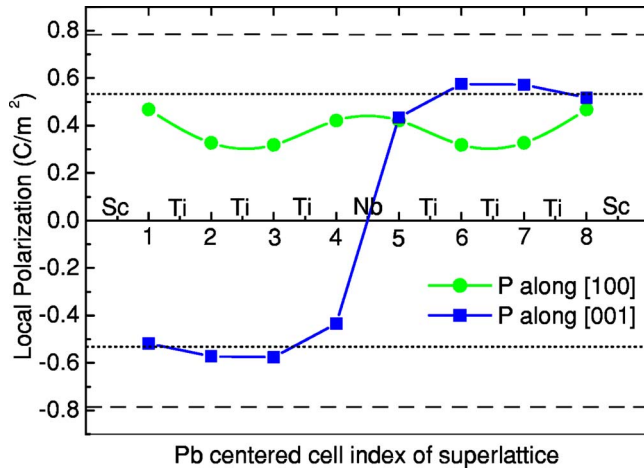
FIG. 3. (Color online) Local polarization profile of the relaxed $Pmm2$ structure. The [001] component changes sign at the dopant layers, while the [100] component is roughly uniform throughout the supercell, giving rise to an overall polarization in the [100] direction. Dotted lines indicate the "ideal" value $0.5e/a^2$; dashed lines represent the spontaneous polarization of bulk tetragonal $PbTiO_3$.

$$\mathbf{P}^{(i)} = \frac{e}{\Omega_c} \sum_\alpha w_\alpha \mathbf{Z}_\alpha^* \mathbf{u}_\alpha^{(i)}, \qquad (1)$$

where i is the Pb-centered unit cell index, α runs over all atoms, and w_α is a weight factor that is unity inside the cell, zero outside, and takes appropriate fractional values for atoms shared with a neighboring cell.[12] For the dynamical effective charge tensors $\mathbf{Z}_\alpha^*$, we use bulk $PbTiO_3$ values of $Z^*(\text{Pb})=3.90$, $Z^*(\text{Ti})=7.06$, $Z_\parallel^*(\text{O})=-5.83$, and $Z_\perp^*(\text{O})=-2.56$ following Ghosez et $al.$[13] We also arbitrarily adopt $Z^*(\text{Nb})=8.06$ and $Z^*(\text{Sc})=6.06$ based on the rough expectation that these atoms should resemble Ti except for a shift by $\pm e$ of the core charge.

The results of this analysis are shown in Fig. 3, which shows the local polarizations in the ground-state $Pmm2$ structure of the superlattice. The local polarization in the [001] direction changes sign across the dopant layers, confirming that HH and TT domain walls are formed. In addition, there is a roughly uniform polarization in the [100] direction, although it is slightly enhanced in the vicinity of the HH and TT domain walls where the [001] polarization is crossing through zero. Thus, the entire superlattice structure is antiferroelectric as concerns the [001] polarizations, but is ferroelectric in the [100] direction. The spontaneous polarization of $P_x=0.36$ C/m^2 computed directly from the LDA calculation compares well with the estimate of 0.38 C/m^2 obtained by averaging the P_x curve in Fig. 3. (The P_z profile of the $P4/mmm$-constrained structure is not shown, but it is almost identical to that of the $Pmm2$ structure.)

In order to understand our results, recall that $PbTiO_3$ has a spontaneous polarization of $0.734e/a^2$, somewhat larger than the ideal value of $0.5e/a^2$ that would give perfect compensation of the donor and acceptor layers. If each domain were to develop its full bulk spontaneous polarization, there would be substantial charges ($\pm 0.47e/a^2$) at the donor layers due to
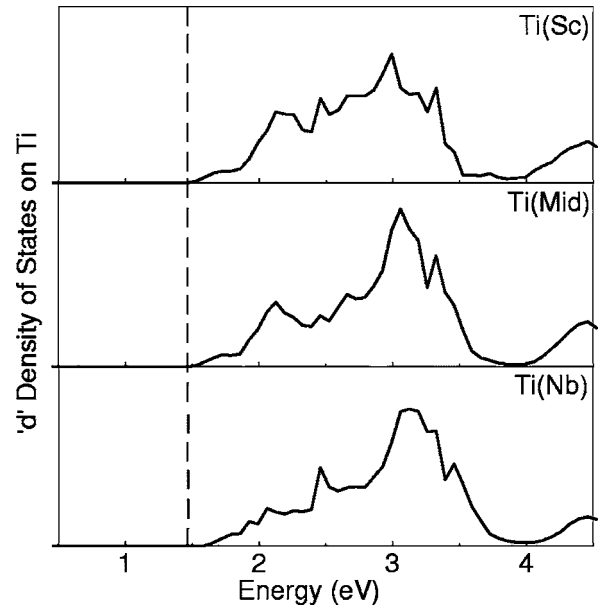

FIG. 4. DOS projected onto three different Ti atoms in the $Pmm2$ supercell. Ti(Sc) denotes the Ti atom in the TiO_2 layer closest to the ScO_2 layer; Ti(Nb) denotes the Ti atom in the TiO_2 layer closest to the NbO_2 layer; and Ti(Mid) denotes a Ti atom in the middle of the supercell, between the two dopant layers.

overcompensation by the domain walls. The resulting depolarizing field would reduce P_z to a value much closer to, but still larger than, the reference value of $0.5e/a^2$. This is precisely what we see in Fig. 3; in the middle of each domain, P_z attains a value just slightly larger than $0.5e/a^2$.

The appearance of the polarization in the in-plane direction can be understood based on the concept of polarization rotation. Many previous works[14] have provided support for a picture in which the crystal is regarded as having a preferred *magnitude* of the polarization, with a rather weak crystalline anisotropy determining its *direction*. If the polarization is prevented from attaining its preferred bulk value in the [001] direction, it can still remain close to this preferred magnitude by tilting off this axis. Indeed, the resulting magnitude of the polarization in the middle layers of the slab, $0.57e/a^2$, is only slightly lower than the preferred bulk value. Moreover, this picture naturally helps explain why the in-plane component of the polarization grows near the HH and TT domain walls, where P_z is in the process of crossing through zero.

Figure 4 gives further evidence of the physical picture outlined above. Here, we have plotted the site-projected DOS for Ti atoms sitting on three different TiO_2 layers of the $Pmm2$ supercell. Specifically, Ti(Nb) is a Ti atom sitting next to the donor-compensated (NB) plane; Ti(Sc) sits next to the acceptor-compensated (Sc) plane; and Ti(Mid) is a Ti atom midway between the two impurity layers. The zero of energy is at the valence-band maximum. The vertical dashed line provides a reference that helps clarify that the spectral weight of the conduction band, and in particular its low-energy edge, shifts to higher energies as one progresses from the Ti(Sc) to the Ti(Nb) layer. The smallness of these shifts confirms that the compensation is quite good, and the small shift that does occur can be attributed to the leftover depo-

larization field in the [001] direction. Furthermore, the sign of this effect is consistent with our previous conjecture that the domain walls are slightly undercompensated.

It is interesting to ask what will happen for superlattices of longer and longer period in the c direction, for a given material system. Unless the compensation is perfect, the depolarizing fields resulting from the imperfect compensation should result in an electrostatic potential having a sawtooth dependence on z. This should be sufficient to close the gap and drive the superlattice structure metallic when the amplitude of this sawtooth potential exceeds the band gap. We can estimate the critical superlattice period for the $PbTiO_3$/Sc/Nb system by recalling that we estimated a net bare charge of $2P_s - e/a^2 \simeq 0.47 e/a^2$ or about 0.51 C/m². Taking the theoretical value of the bulk band gap of E_g = 1.8 eV and a bulk dielectric constant of about 110, we estimate that the depolarization field would close the band gap when the distance L between impurity layers exceeds a critical value of about 75 Å or about 19 $PbTiO_3$ layers.

If it is desired to increase the superlattice period and still keep an insulating structure, then the precision of the compensation should be improved. Two approaches suggest themselves. First, one could make use of mixed dopant layers of composition $Ti_{1-x}Sc_x$ or $Ti_{1-x}Nb_x$, with x tuned to obtain the correct degree of compensation for a given bulk material. Second, the bulk material itself may be varied in order to adjust its spontaneous polarization closer to the ideal value of $0.5e/a^2$. For example, replacing $PbTiO_3$ by $PbZr_xTi_{1-x}O_3$ (PZT) with $x \simeq 0.2$ may accomplish this.[15] Using such strategies, it may be possible to construct long-period insulating superlattices, perhaps even with periods large enough to be of use for optical grating applications.

In summary, we have calculated the properties of a particular realization of a hypothetical class of ferroelectric superlattice structures containing head-to-head and tail-to-tail 180° domain walls compensated and stabilized by the intentional insertion of atomic charged-impurity layers. In the system we chose for study, in which Sc and Nb substitutional layers provide the compensation in $PbTiO_3$, the spontaneous polarization of the bulk material is larger than the ideal value; consequently, the superlattice develops an in-plane ferroelectric polarization, while also developing the expected antiferroelectric domain structure in the growth direction. This appears to be a way of forcing polarization rotation into the in-plane orientation in $PbTiO_3$, and it would be interesting to explore how the superlattice properties (spontaneous polarization, Curie temperature, etc.) could be tuned by the growth conditions (e.g., superlattice period). More generally, it would be interesting to investigate other host perovskite ferroelectric materials, other kinds of compensating layers (including, perhaps, dopants from column II or VI of the periodic table), and alloy compositions of the bulk and/or dopant layers. With a more suitable matching of the compensation, the driving force for polarization rotation could be reduced, and a true $P4/mmm$ superlattice structure could presumably be stabilized. In fact, it also seems possible that a normally rhombohedral bulk ferroelectric like $BaTiO_3$, whose spontaneous polarization is *smaller* than the ideal value of $0.5e/a^2$, could have its polarization rotated in the opposite way, into alignment with the z-axis, since in this case the compensating layers would enhance the polarization in that direction. Finally, much longer-period superlattices might be obtained by very accurate matching of the compensation. There are thus many open avenues for future theoretical and experimental studies.

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