Theoretical investigation of polarization-compensated II-IV/I-V perovskite superlattices

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Recent work suggested that head-to-head and tail-to-tail domain walls could be induced to form in ferroelectric superlattices by introducing compensating "delta doping" layers via chemical substitution in specified atomic planes [Phys. Rev. B **73**, 020103(R), 2006]. Here we investigate a variation of this approach in which superlattices are formed of alternately stacked groups of II-IV and I-V perovskite layers, and the "polar discontinuity" at the II-IV/I-V interface effectively provides the delta-doping layer. Using first-principles calculations on $SrTiO_3/KNbO_3$ as a model system, we show that this strategy allows for the growth of a superlattice with stable polarized regions and large polarization discontinuities at the internal interfaces. We also generalize a Wannier-based definition of layer polarizations in perovskite superlattices [Phys. Rev. Lett. **97**, 107602 (2006)] to the case in which some (e.g., KO or NbO_2) layers are non-neutral, and apply this method to quantify the local variations in polarization in the proposed $SrTiO_3/KNbO_3$ superlattice system.

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Ferroelectric materials have been the subject of increasing theoretical and experimental study in recent years. In particular, multicomponent superlattices based on ABO_3 perovskites have been shown to possess many interesting properties (see Ref. 1 and references therein). Currently, heterointerfaces between different ABO_3 perovskites are also the subject of intense investigation.[2,3,4,5,6] Given the huge number of possible superlattice arrangements, it is prudent to investigate systems of potential interest using first-principles calculations to confirm a given system possesses the desired properties before experimental work is performed.[7,8]

In recent work, Wu and Vanderbilt[9] introduced a novel concept in which 180° head-to-head (HH) and tail-to-tail (TT) domain walls are induced to form in a ferroelectric superlattice via the insertion of compensating "delta doping" layers. For example, in a II-IV ABO_3 perovskite, column III or V ions could replace the IV ions in one BO_2 layer, inducing the formation of a HH or TT domain wall respectively. Usually the formation of a HH or TT domain wall perpendicular to the polarization direction would entail an unacceptable Coulomb energy cost, or cause the domain wall to become metallic in order that free carriers could compensate the domain wall. However, it was shown that the delta-doping layers could be arranged to compensate the polarization bound charge and allow a structure in which the ferroelectric domains are polarized in opposite directions and are separated by HH and TT domain walls.

Here we examine the possibility of forming a multicomponent perovskite superlattice with similarly large discontinuities in the local electric polarization by making use of alternating II-IV and I-V perovskite constituents. In this case, the "polar discontinuity" associated with the II-IV/I-V interface plays the role of delta-doping layer and compensates the polarization bound charge at the interface. (Clearly a similar strategy could be applied to II-IV/III-III perovskite superlattices.) The resulting structure is not switchable, but is locally polarized and has strongly broken inversion symmetry. We demonstrate this concept via first-principles calculations on $SrTiO_3/KNbO_3$ as a prototypical system, showing successful compensation and robust formation of locally polarized regions. Superlattices of this type are shown to remain insulating to rather large layer thicknesses. Finally, we clarify how the Wannier-based definition of layer polarization in perovskite superlattices introduced in Ref. 10 can be generalized for a system having non-neutral AO or BO_2 constituent layers, and apply this to the $SrTiO_3/KNbO_3$ system to map out the local variations in polarization.

The type of superlattice structure we have in mind is illustrated in Fig. 1. Here, two unit cells of $KNbO_3$ (in the sequence NbO_2–KO–NbO_2–KO) repeatedly alternate with two unit cells of $SrTiO_3$ (in the sequence TiO_2–SrO–TiO_2–SrO) during growth. While each added $KNbO_3$ or $SrTiO_3$ unit cell is neutral, in $KNbO_3$ this neutrality results from the cancellation of charges on the KO^- and NbO_2^+ layers, while in $SrTiO_3$ the individual layers are neutral. When the layers are assembled as in Fig. 1, the presence of the "polar discontinuity" introduces effective compositional charges of $\pm 1/2$ at the NbO_2/SrO and TiO_2/KO interfaces respectively, as shown. Similar effects have recently been extensively discussed for $SrTiO_3/LaAlO_3$ and related interfaces.[2,3,4,5] Intuitively, we may regard each KO^- layer in bulk $KNbO_3$ as being half-compensated from each of its two immediate NbO_2^+ neighbors, whereas at the TiO_2/KO interface the KO^- is only half-compensated because it has only a single NbO_2^+ neighbor. The resulting compositional charge densities are $\sigma_{\rm comp} = \pm e/2a^2$ at the NbO_2/SrO and TiO_2/KO interfaces respectively.

Two possibilities for cancelling these compositional charges in a I-V/II-IV superlattice are shown in Fig. 2. In Fig. 2(a) we assume that both I-V and II-IV materials are ferroelectrics, and to take an extreme case we assume

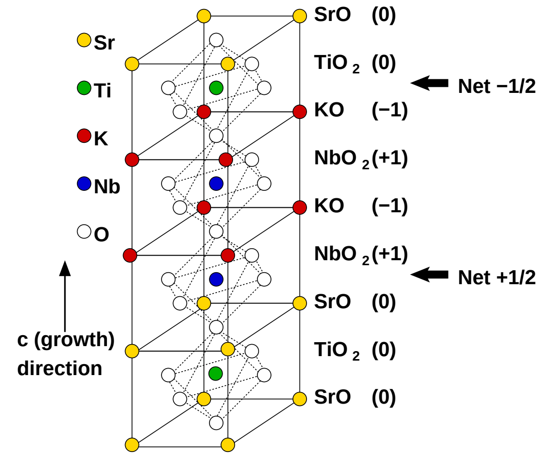

FIG. 1: (Color online) Sketch of a possible II-IV ($SrTiO_3$) / I-V ($KNbO_3$) superlattice grown along [001].

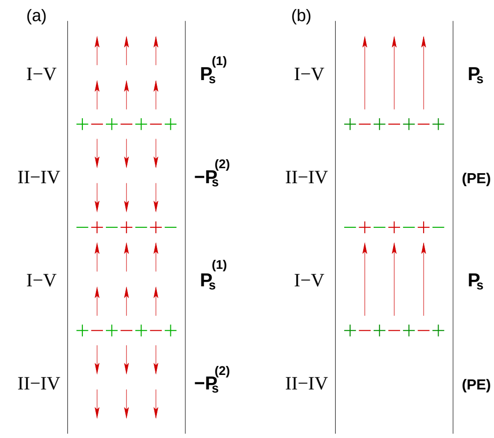

FIG. 2: (Color online) Two possible II-IV/I-V superlattice arrangements yielding compensating heterointerfaces and stabilized ferroelectric discontinuities. (a) Both materials are ferroelectric, with antiparallel polarizations along the growth direction. (b) One material is paraelectric and the other ferroelectric. Green and red interface charges denote polar-discontinuity and polarization-induced charges, respectively.

their spontaneous polarizations are equal ($P_s^{(1)} = P_s^{(2)}$) at the specified in-plane lattice constant. Arranging the polarizations so that they alternate up and down as shown, the ideal compensation $\sigma_{\rm bound} + \sigma_{\rm comp} = 0$ between polarization bound charge and compositional interface charge is realized when $P_s^{(1)} = P_s^{(2)} = e/4a^2$. A second scenario, shown in Fig. 2(b), would result from the alternation of I-V and II-IV materials, only one of which is ferroelectric, while the other is paraelectric. In this case, ideal compensation requires $P_s = e/2a^2$ for the ferroelectric component. Intermediate cases, with the alternation of a strong and a weak ferroelectric, are also possible.

In the remainder of this paper, we focus on the scenario sketched in Fig. 2(b) as realized in the $SrTiO_3/KNbO_3$ superlattice system, using density-functional calculations to demonstrate the compensation mechanism proposed above. The choice of $SrTiO_3$ as the II-IV paraelectric component is motivated by the fact that it is a well-studied material[11,12] and by the common use of $SrTiO_3$ as a substrate for growth of thin perovskite films. With this in mind, we assume coherent epitaxy of our superlattices on $SrTiO_3$, so that the in-plane lattice constants are constrained to the experimental value $a_0 = 3.905$ Å of bulk $SrTiO_3$. As explained above, ideal compensation would require that the ferroelectric I-V component should have a spontaneous polarization of $P_s = e/2a_0^2 = 0.525\,C/m^2$. We have chosen $KNbO_3$ for the I-V component because it provides a reasonable match to this value. While bulk $KNbO_3$ is a rhombohedral ferroelectric with polarization along (111) at low temperature, its lattice constant is nearly 3% larger than that of $SrTiO_3$. The calculations of Diéguez *et al.*[13] have shown that $SrTiO_3$ should become a tetragonal ferroelectric with polarization along (001) when compressed in-plane to fit to the $SrTiO_3$ lattice constant. Moreover, those same calculations indicated that the polarization of $KNbO_3$ would be $\sim 0.45\,C/m^2$ under these conditions, which is fairly close to the target value. $KNbO_3$ also has the advantage of being a commonly used and very well-studied I-V perovskite.[11,12]

The open-source plane-wave density-functional code PWSCF[14] was used for the calculations, with the local-density approximation to exchange and correlation[15] and use of ultrasoft pseudopotentials.[16] Because we have no reason to expect the appearance of in-plane polarization components in this system (see above), we have assumed tetragonal P4*mm* symmetry throughout.

We first calculate the theoretically optimized value of the lattice constant a_0 for bulk $SrTiO_3$ using an $8\times8\times8$ k-point grid and a plane-wave energy cutoff of 30 Rydberg, obtaining a value of value of 3.849 Å. This leads to a theoretical ideal matching condition of P_s=0.54 C/m^2. Using the same k-point grid and cutoff to study bulk $KNbO_3$ in P4*mm* symmetry with its in-plane lattice constant constrained to this a_0, we calculate its spontaneous polarization to be 0.42 C/m^2. These results are in good agreement with previous work.[13]

Of primary importance is whether the compensation of the bound charge is sufficient to maintain the insulating nature of the system as the supercell size is increased. We consider superlattices consisting of n unit cells of $SrTiO_3$ alternating with n unit cells of $KNbO_3$, so that the supercell contains $10n$ atoms. Figure 1 illustrates the case of n=2. Relaxations of the multilayered supercells are performed for values of n ranging from 1 to 5. The plane-wave energy cutoff is 30 Rydberg in all cases, and the k-point grid is $8\times8\times M$ with $M = 4$ for $n = 1$ and $M = 2$ for $n \geq 2$.

We find that the system remains insulating in all these cases. The density of states for $n = 2$ is shown in Fig. 3, showing a clear gap between valence and conduction band states. There is, however, a gradual closing of the band

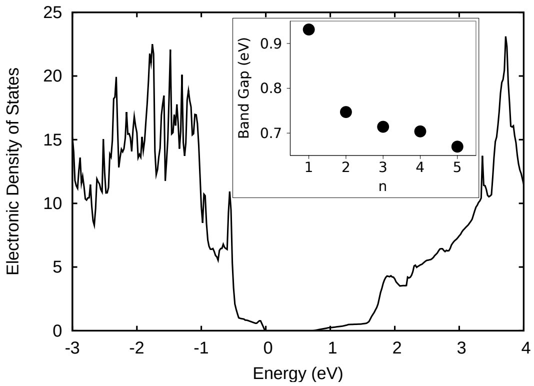

FIG. 3: Calculated electronic density of states for a supercell with $n = 2$ (two $SrTiO_3$ layers and two $KNbO_3$ layers). Inset shows the the gradual reduction of band gap for $n SrTiO_3/n KNbO_3$ supercells as n increases.

gap as n is increased, as may be expected from the imperfect charge compensation. The calculated band gap as a function of the supercell size is shown in the inset to Fig. 3. The results for $n \geq 2$ suggest a nearly linear decrease in band gap with increasing n. This reduction is rather modest; a simple linear extrapolation suggests that the system would not become metallic until $n \simeq 32$.

In order to understand the resulting local polarizations in these multilayered systems, it is useful to start from a simple model and test whether its predictions are borne out by a more detailed analysis. Due to the imperfect compensation in the system, if one starts by assembling regions of spontaneously polarized $KNbO_3$ alternating with regions of unpolarized $SrTiO_3$, one finds planar charge densities $\pm\sigma$ at the interfaces, with $\sigma = P_{\rm s} - e/2a^2 = -0.12\,{\rm C/m}^2$. Assuming that the screening of this charge can be treated using a linear dielectric analysis and that the thicknesses of the two constituents are approximately the same, one finds a screened charge density of $\sigma_{\rm scr} = 2\sigma/(\epsilon_1+\epsilon_2)$, where $\epsilon_{1,2}$ are the dielectric constants of $KNbO_3$ and $SrTiO_3$ respectively. The screened polarizations then become $P_{\rm KNbO_3} = P_s - \sigma(\epsilon_1 - 1)/(\epsilon_1+\epsilon_2)$ and $P_{\rm SrTiO_3} = \sigma(\epsilon_2 - 1)/(\epsilon_1+\epsilon_2)$. Since $\sigma < 0$, we expect $P_{\rm KNbO_3}$ to be enhanced slightly beyond its spontaneous value, and $P_{\rm SrTiO_3}$ to have a small value of the opposite sign.

To investigate the correctness of this picture, we perform more precise calculations of the local polarization profile. An accurate method for obtaining layer polarizations was introduced in Ref. 10, where a one-dimensional Wannier analysis[17] was employed. To do this, the overlap matrices $M^{(k)}_{mn} = \langle u_{mk}|\, u_{n,k+b}\rangle$ between neighboring k-points along strings in the $\hat{z}$ direction are computed, where u_{mk} is the periodic part of the Bloch function ψ_{mk}. The singular value decomposition $M = V\Sigma W^\dagger$ is used to obtain $\tilde{M} = UW^\dagger$, which is exactly unitary. The eigenvalues λ_m of the product $\Lambda = \prod \tilde{M}^{(k)}$ of these matrices along the k-point string yield the Wannier centers as $z_m = (-c/2\pi)\,{\rm Im}\,\ln\lambda_m$. These Wannier centers form into "sheets" of charge that are localized in the growth direction but delocalized in the plane. For each layer j, we define the layer center $z_{0,j}$ to be the average position of the ions associated with that layer. The "intralayer polarization" is then given by

$$p^{\rm il}_j = \frac{1}{S}\sum_{\tau\in j} Q_\tau R_{\tau z} - \frac{2e}{S}\sum_{m\in j} \bar{z}_m, \qquad (1)$$

where $S = a^2$ is the basal cell area, Q_τ is the core charge of ion τ belonging to layer j, $R_{\tau z}$ is the position of the ion measured relative to $z_{0,j}$, and $\bar{z}_m$ is the position of the Wannier center z_m relative to $z_{0,j}$ after a k_x and k_y average over wavevector strings.

As long as each layer is neutral, the total polarization of the supercell can be obtained just as $(\sum_j p^{\rm il}_j)/c$ where c is the supercell lattice constant, because the dipole moment of a neutral layer is independent of origin. For a supercell containing charged layers like those associated with an I-V material, this sum needs to be modified to $(\sum_j p^{\rm il}_j + \sigma_j z_{0,j})/c$ in order to remain meaningful as a total polarization. Here $\sigma_j = \pm e/S$ for a NbO_2 or KO layer respectively, or 0 for a TiO_2 or SrO layer. However, the second term does not take the form of a sum over layer contributions. To cast the sum into this form, we define a layer-offcentering polarization $p^{\rm lo}_j$ that reflects the displacement of the layer charge σ_j from the average position of its neighbors according to

$$p^{\rm lo}_j = \sigma_j \left(\frac{1}{2}\,z_{0,j} - \frac{1}{4}\,z_{0,j-1} - \frac{1}{4}\,z_{0,j+1} \right). \qquad (2)$$

In an extended region of I-V layers, the sum $\sum_j p^{\rm lo}_j$ counts each charged layer once and only once, but this counting is violated at the interfaces with the II-IV layers. For example, at a NbO_2/SrO interface, we have not accounted for a charge density of $e/4S$ in the last NbO_2 layer, and we have incorrectly assigned a charge of $-e/4S$ to the first SrO layer. The missing charge is equivalent to a charge density of $e/2S$ located midway between the $z_{0,j}$ values of these two layers. Similarly, a TiO_2/KO interface is assigned a charge $-e/2S$ located halfway between these layers. Thus, the total polarization of the supercell can finally be written as $(\sum_j [p^{\rm il}_j + p^{\rm lo}_j] + \sum_\mu z^{\rm int}_\mu \sigma^{\rm int}_\mu)/c$, where $z^{\rm int}_\mu$ and $\sigma^{\rm int}_\mu$ are the positions and charges of the extra interface charges.

The charges $\sigma^{\rm int}_\mu$ are, of course, nothing other than the compositional polar discontinuity charges $\sigma_{\rm comp}$ discussed earlier. Having accounted for these, we are left with total layer polarizations $p_j = p^{\rm il}_j + p^{\rm lo}_j$ associated with each layer, which thus provide a layer-by-layer picture of the polarization in this type of system. To convert these into local polarizations P_j having units of charge per unit area, we let $P_j = p_j/c_j$ where $c_j = (z_{0,j+1} - z_{0,j-1})/2$.

The results for $n = 4$ are shown in Fig. 4. These are very indicative of the results obtained for all the supercell

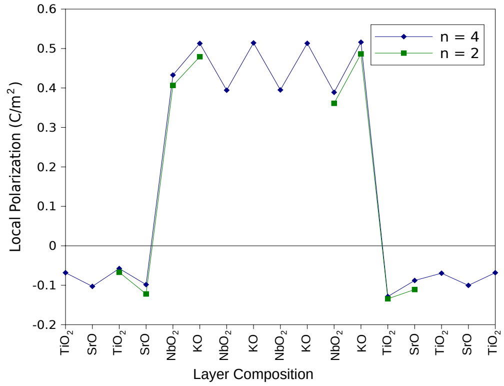

FIG. 4: (Color online) Layer-by-layer local polarization profile of a supercell with $n = 4$ (four $SrTiO_3$ units and four $KNbO_3$ units), with corresponding results for $n = 2$ also indicated near each of the interfaces.

sizes examined. The results for $n = 2$ centered on each interface are also shown on the corresponding segments in the figure, allowing the similarity in the behavior of the layer polarization to be clearly seen. A saw-tooth–like variation about an approximately constant value is evident in examining layers belonging to a single ABO_3 constituent. The polarization of the AO layer is larger in magnitude than the BO_2 in both the I-V and II-IV materials in the system, as has been observed elsewhere.[10] However, there is a noticeable modification of the TiO_2 layer that is adjacent to KO at the TiO_2/KO heterointerface; the polarization of this layer is enhanced, so that the saw-tooth behavior is broken.

We find the average polarization deep in the $KNbO_3$ region to be about $0.45\,C/m^2$, while in the $SrTiO_3$ region it is about $-0.08\,C/m^2$. Recalling that P_s of bulk $KNbO_3$ at this in-plane lattice constant was found to be $0.42,C/m^2$, we find that our earlier expectations for the behavior of the polarization profile, that P_{KNbO_3} should be enhanced relative to its bulk P_s while P_{SrTiO_3} should be small and of opposite sign, are clearly confirmed.

In summary, our calculations on perovskite superlattices composed of II-IV and I-V components have shown that sharp local polarization discontinuities can be stabilized at the charged heterointerfaces that are intrinsic to such superlattices. Focusing on the $SrTiO_3/KNbO_3$ system, our calculations show that while the charge compensation is not perfect, the superlattice period can be increased to rather large dimensions before the remaining uncompensated bound charges drive the system metallic. The same principles should apply to II-IV/III-III perovskite superlattices. By suitable choice of materials, and/or by tuning the polarization via the application of epitaxial strain, which can have a strong effect on the spontaneous polarization,[13] it should be possible to obtain even better compensation. The resulting superlattices have strongly broken inversion symmetry, and may be of interest for piezoelectric, pyroelectric, non-linear optical, and other applications. Finally, we have also demonstrated how a layer-by-layer Wannier analysis may be applied to a perovskite system in which non-neutral layers are present, as an important step towards a more complete understanding of the local behavior of multilayered superlattices.

Acknowledgments

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