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Origin of reduced polarizations in short-period BaTiO$_3$/SrTiO$_3$ ferroelectric superlattices

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We present an analysis of the polarization properties of BaTiO$_3$/SrTiO$_3$ superlattices using an effective Hamiltonian derived from first-principles calculations based on density-functional theory. We show that the hardening and modification of local soft modes at the interface environment is responsible for (a) the deviation of the interface structure from the bulk one and (b) the suppression of polarization in the short-period superlattices. The effect of this interfacial coupling is shown to be enhanced as the epitaxial strain becomes tensile. © 2009 American Institute of Physics. [DOI: 10.1063/1.3056388]

The enhancement of ferroelectric polarization in thin films is still an important issue in their device applications. Experimental breakthrough in the layer-by-layer growth technique of heterostructure oxide superlattices has triggered intensive exploration of physical properties of artificially grown perovskite oxide superlattices.\textsuperscript{1–5} Recent fabrication of ultimately short unit-cell period superlattices consisting of ferroelectric perovskite BaTiO$_3$ (BTO), SrTiO$_3$ (STO), and CaTiO$_3$ layers has made it possible to examine the effect of layer stacking and lattice constraint on the physical properties of perovskite superlattices thereby contributing to the understanding of fundamental mechanisms of ferroelectricity in oxide superlattices.\textsuperscript{6}

In spite of the rapid progress in experiments, research activities toward the polarization enhancement of thin films have been hampered by various problems including defects in the film or tunneling current between the surrounding electrodes in addition to the strain control. Even if a significant enhancement is expected from the lattice strain by the substrate, the polarization of thin films in practice often turns out to be smaller than that of its bulk state material.\textsuperscript{7,8} For instance, the (BTO)$_{15}$(STO)$_3$ superlattice on the STO substrate, imposing a compressive in-plane stress to the BTO layers, was reported to give an increase in polarization over that in the BTO single phase film, but far less than that in the bulk BTO polarization.\textsuperscript{3}

While the lattice strain is known to be one of the key control parameters in determining the ferroelectric polarization of superlattices, the ferroelectric couplings between constituent layers are not well understood beyond a macroscopic electrostatic model,\textsuperscript{9,10} which may not apply to the short-period superlattices with a few layer thick unit cell. Recently there have been experimental and theoretical studies reporting the absence of enhanced ferroelectricity in the short-period superlattices.\textsuperscript{5,11,12} So far there is no clear understanding on the microscopic origin of this reduced polarization in the short-period superlattice. In this paper, we present an effective Hamiltonian analysis based on the first-principles calculations of (BTO)$_n$(STO)$_n$ to explain the origin of their reduced polarization with decreased periodicity.

To carry out the first-principles calculations for the (BTO)$_n$(STO)$_n$ superlattices, we used the plane-wave basis density-functional-theory (DFT) code and the Vienna ab initio simulations package (VASP),\textsuperscript{13,14} within the local-density approximation. For the construction of the effective Hamiltonian for the BTO/STO superlattices, we took account of the low energy modes. The Ti-centered local mode $\xi_i$ corresponding to the lowest TO$_1$ mode ($I_{15}$ soft mode) and elastic strain $\eta_i$ corresponding to the long wavelength acoustic mode among the phonon modes of cubic perovskite oxides.\textsuperscript{15} Since we focus primarily on the ferroelectric distortions along the $c$-direction, the degrees of freedom can be further reduced down to the displacements TO$_1$ and acoustic modes along the $c$-axis only, as in-plane strain is fixed. The calculational details are provided in Ref. 16. In our previous work,\textsuperscript{16} we used an average model of the effective Hamiltonian for an interface in the (BTO)$_n$(STO)$_m$ superlattice with $n+m=5$, where the local parameters for the Ti layers sandwiched by BaO and SrO layers $A_i$, $B_i$, $C_i$, $Z_i$, and $g_i$ were taken as an average of the corresponding parameters of the two neighboring components. The obtained results of the average model for $n+m=5$ were shown to be in good agreement with those of the first-principles calculations.

However, this average model approach fails when it is applied to the short-period superlattices like (BTO)$_1$(STO)$_1$. Figure 1(a) demonstrates that the difference between the average model and the first-principles becomes amplified as $n$ approaches 1 in (BTO)$_n$(STO)$_n$. This behavior can be related to the interface fraction, i.e., the ratio of the interface layers over the total layers. For instance, the interface fraction of (BTO)$_1$(STO)$_4$ is $2/5=40\%$, while that of (BTO)$_4$(STO)$_1$ is $2/2=100\%$. Thus it is certain that the average model does not work for (BTO)$_1$(STO)$_1$ because the interface contribution is dominant.

One can think of two possible causes for the discrepancy between the average model and the first-principles results: (i) the presence of a linear term in $\xi_i$ and (ii) a modification of

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the local self-energy at the interface. To find out the effect of the linear term, which should be allowed by the broken inversion symmetry at the interface, we have calculated the forces at the BTO/STO interface from first-principles and estimated its effect by solving the effective Hamiltonian. From the results, it was shown that the linear term at the BTO/STO interface is not significant numerically and does not affect the local polarization.

The modification of the local self-energy can have contributions from either a stiffening of the quadratic term or a modification of the soft mode itself due to the interface. Although it is difficult to sort out each contribution to the local self-energy term, it is obvious to see that the bulk local mode $\xi_i$ for either BTO or STO is no longer a proper eigenmode at the BTO/STO interface due to the change in local environment at the interface. Indeed this modified polar distortion at the interface is expected to give rise to a renormalization of the self-energy with a sizable change in the interface fraction is large compared to that of the ferroelectric BTO components.

To verify this idea, we performed DFT calculations for the TO$_1$ phonon eigenvector of the BTO$_1$/STO$_1$ superlattice and found that the local mode $\xi_i$ of the BTO/STO interface consists of a mixture of the lowest energy TO mode with higher energy phonon modes of the bulk BTO and STO, respectively, as illustrated in Fig. 2. Quantitatively, we can represent the local mode $\xi_i^I$ of the BTO/STO interface in terms of other phonon modes of bulk BTO and STO, respectively,

$$\left| \xi_i^I \right> = 0.98|\xi_B(\text{TO}_1)> + 0.09|u_B(\text{TO}_2)> + 0.13|u_B(\text{TO}_3)> + 0.96|\xi_S(\text{TO}_1)> + 0.22|u_S(\text{TO}_2)> + 0.18|u_S(\text{TO}_3)>,$$

where the subscripts $B$ and $S$ represent the bulk BTO and STO, respectively, and the superscript $I$ the BTO/STO interface.

In order to investigate the change in the local self-energy due to the interface, we determined total energies with respect to the local mode distortions of the BTO bulk, STO bulk, and BTO$_1$/STO$_1$ superlattice soft eigenmode, respectively. In addition, we defined a bulk-average local mode by taking an average of the bulk BTO and STO local modes and calculated the total energy curve of the bulk-average mode in the BTO$_1$/STO$_1$ superlattice. The calculated energy curve of the bulk-average mode is compared with that of the BTO bulk, STO bulk, and BTO$_1$/STO$_1$ superlattice local modes in Fig. 3. Further, we have the energy curve obtained from the average of BTO and STO $A_i$ coefficients in Fig. 3(a). The stiffening of the bulk-average local mode relative to the energy curve of the average $A_i$ coefficients indicates a large correction to the phonon frequency due to the BTO/STO interface environment.

From the total energy curves in Fig. 3(a), however, one notices that the bulk-average local mode is slightly stiffer than the soft eigenmode of the BTO$_1$/STO$_1$ superlattice. This minor difference reflects the change in the bulk-average mode itself to the interface local mode at the interface layer. The modification of the local mode can be attributed to the

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**FIG. 1.** (a) Comparison of the polarizations of (BTO)$_n$/STO)$_n$ calculated by the average model (open circle), the effective Hamiltonian with interface correction (filled circle), and the first-principles calculations (diamond) with respect to the bulk BTO polarization $P_0$. We took the reference $P_0 = 22.7$ $\mu$C/cm$^2$ for the effective Hamiltonian and $P_0 = 26.9$ $\mu$C/cm$^2$ for the first-principles calculations, respectively. (b) Strain dependence of the polarizations of (BTO)$_n$/STO$_n$ and (BTO)$_n$/STO$_n$ superlattices as obtained from the average model and the current model with the interface corrections.

**FIG. 2.** (Color online) Schematic representation of the TO phonon modes in BTO (down), STO (up), and (BTO)$_n$/STO$_n$ (center). Large (red) circle corresponds to Ba, medium (blue) circle to Sr, small dark (black) circle to Ti, and small open (white) circle to O. Numbers beside the bold arrows represent the displacements of each TO mode, and numbers beside the dotted arrows indicate the participation of the bulk BTO and STO modes in the TO$_1$ mode of (BTO)$_1$/STO$_1$. 

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**FIG. 3.** The energy curves obtained from the average of BTO and STO $A_i$ coefficients in Fig. 3(a). The stiffening of the bulk-average local mode relative to the energy curve of the average $A_i$ coefficients indicates a large correction to the phonon frequency due to the BTO/STO interface environment.
coupling of the local soft mode to the higher energy phonon mode. Since the bulk-average mode is not a proper eigenmode at the interface, the coupling of the bulk-average mode with the higher energy phonon can give rise to an effective softening contribution to the interface local self-energy.

Following the fitting procedure prescribed in Ref. 16, we could obtain the local parameters \( A_i \) and \( B_i \) for the modified local mode at the BTO/STO interface. As listed in Table I, the harmonic term \( A_i \) at the interface exhibits a large deviation from that of the BTO and STO average, whereas the anharmonic term \( B_i \) remains close to that of the BTO and STO average. Consequently the modification of the local self-energy at the interface leads to the polarization reduction, which is quite significant when the interface fraction increases, i.e., \( n \to 1 \) in the \( (\text{BTO})_n/(\text{STO})_n \) superlattice. The close agreement of the results of the effective Hamiltonian including the local self-energy correction through the first-principles calculations [see Fig. 1(a)] highlights the crucial role of the hardening of the bulk-average mode and its modification at the interface layer due to the coupling to the higher energy phonon mode.

We also investigated the effect of epitaxial strain on the interface contribution. To capture the effect of epitaxial strain, we added an in-plane strain energy \( \mathcal{H}_{\text{epi}} = \sum \alpha \xi \eta + \eta \eta \) to the elastic energy term in Eq. (1), where \( \alpha \) is 44 eV for BTO and 43 eV for STO. We find that the coupling of local modes with the epitaxial in-plane strain is much smaller, i.e., \( g_{\alpha}^i = -2.4 \) and 3.1 eV/Å\(^2\) for BTO and STO, than the coupling with the out-of-plane strain, i.e., \( g_{\beta}^i = 92 \) and 59 eV/Å\(^2\) for BTO and STO, respectively.\(^{16}\) Analysis of \( \mathcal{H}_{\text{eff}} \) shows that (a) the polarization \( P \) reduces with tensile strain for all superlattices, consistent with results of earlier first-principles calculations\(^{17}\) and (b) the effect of interfacial term becomes strongly enhanced with tensile strain [see Fig. 1(b)].

In conclusion, we showed that the hardening of the bulk-average local mode and the modification of the local soft mode at the interface of BaTiO\(_3\)/SrTiO\(_3\) is responsible for the reduced polarization of the short-period epitaxial ferroelectric superlattices. The weakened ferroelectric instability is attributed to the renormalization of the local self-energy term \( A_i \), which is essential in the effective Hamiltonian description of the oxide superlattices with a sizable interface fraction. The sensitivity of polarization of the short-period superlattice in response to the epitaxial strain suggests that the choice of the substrate is crucial in determination of the ferroelectric properties of oxide superlattices.

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