

# First-principles calculation of the band offset at BaO/BaTiO<sub>3</sub> and SrO/SrTiO<sub>3</sub> interfaces

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We report first-principles density-functional pseudopotential calculations on the atomic structures, electronic properties, and band offsets of BaO/BaTiO<sub>3</sub> and SrO/SrTiO<sub>3</sub> nanosized heterojunctions grown on top of a silicon substrate. The density of states at the junction does not reveal any electronic induced interface states. A dominant perovskite character is found at the interface layer. The tunability of the band offset with the strain conditions imposed by the substrate is studied. Using previously reported theoretical data available for Si/SrO, Si/BaO, SrTiO<sub>3</sub>/Pt, and BaTiO<sub>3</sub>/SrRuO<sub>3</sub> interfaces we extrapolate the band alignments along two gate stacks of technological interest: Si/SrO/SrTiO<sub>3</sub>/Pt and Si/BaO/BaTiO<sub>3</sub>/SrRuO<sub>3</sub> heterostructures.

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## I. INTRODUCTION

The search for alternative gate dielectric materials to replace silica (SiO<sub>2</sub>) in microelectronic devices is one of the grand challenges that the materials science community and the Si-based semiconductor industry are facing at the current time.<sup>1</sup> The rapid scaling of the physical gate lengths of metal-oxide-semiconductor field-effect transistors (MOSFET's) requires a concomitant rapid reduction of the gate dielectric thickness in order to preserve a high gate oxide capacitance. This can no more be accomplished by lowering the size of the SiO<sub>2</sub> layer because, together with problems in thickness control, the leakage current would become inacceptably high. Indeed, the leakage current from the channel to the gate is due to the direct tunneling of carriers and increases exponentially with the decrease of both the thickness of the gate dielectric and the height of the electrostatic barrier for the electrons through the gate stack. The current road-map projection [assessed by the the International Technology Roadmap for Semiconductors (ITRS) (Ref. 2)] imposes the choice of an alternative gate dielectric with a good capacitance for a thick-enough layer and its full implementation into the production line by 2005.

The properties that the new dielectric should meet are well established and have been reviewed recently by Wilk and Wallace.<sup>3</sup> They can be divided into *fundamental material properties* and *device processing and performance properties*. Among the material properties, we can enumerate (i) a higher dielectric constant than amorphous silica ( $\kappa_{\text{SiO}_2} = 3.9$ ) in order to increase the capacitance without decreasing the thickness, (ii) large band gaps and band offsets with Si to prevent tunneling currents, (iii) a good thermodynamic stability in contact with the Si substrate, (iv) a good quality of the interface with the Si channel, which means a small number of electrical defects and a low midgap interface state density, and (v) film morphology avoiding the formation of polycrystalline films and grain boundaries. Among the device properties, we can cite (vi) a good compatibility with metallic gate electrodes, (vii) a compatibility with the deposition mechanism during the fabrication process, and (viii) reliability.

Many materials satisfy some subset of the previous criteria, but the identification of a dielectric that addresses *simultaneously* all of the requirements is a real challenge. Investigations on oxides like Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, HfO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub>, Y<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> have given encouraging results in the last few years.<sup>4</sup> Among the most promising candidates, *AB*O<sub>3</sub> perovskite oxides (where *A* stands for Ba or Sr and *B* stands for Ti) appear in good position.

The *AB*O<sub>3</sub> compounds have a dielectric constant above 300, one order of magnitude higher than the other candidates. Although they are thermodynamically unstable in direct contact with Si (they react to form titanium silicide and alkaline-earth silicate<sup>4,5</sup>), they can be grown in perfect registry with the Si substrate by means of molecular beam epitaxy (MBE) when including a silicon-compatible buffer layer. On the one hand, this layer must be sufficiently thick to ensure the physical separation between the substrate and perovskite. On the other hand, it must remain thin enough to keep the benefit of the high dielectric constant of the *AB*O<sub>3</sub> compound (the capacitance of the lower- $\kappa$  buffer layer being in series with that of the perovskite).

In the McKee-Walker process,<sup>6-8</sup> the buffer consists in few atomic layers of *A*O alkaline-earth oxide that can eventually be alloyed during the growth in order to accommodate the lattice mismatch with Si. The growth of *A*O on Si includes the presence, at the interface, of a (sub)monolayer of *A*Si<sub>2</sub> silicide so that the final structure corresponds to the sequence Si/*A*Si<sub>2</sub>/*A*O/*AB*O<sub>3</sub>. The epitaxy is such that *AB*O<sub>3</sub>(001)||*A*O(001)||Si(001) and *AB*O<sub>3</sub><110>||*A*O<100>||Si<100>; i.e., the *AB*O<sub>3</sub> atomic planes are rotated 45° around the (001) *A*O direction.<sup>9</sup> The epitaxial crystalline growth at the oxide/semiconductor interface avoids the formation of defects and ensures the continuity of the dielectric displacement.<sup>7</sup> MBE techniques allow the control of the growing sequence at the submonolayer level preventing grain boundaries and providing a good quality interface and extremely smooth surface morphology.

First attempts to make MOSFET's including perovskite oxides have been reported recently. Using a 110-Å-thick SrTiO<sub>3</sub> layer as the gate dielectric, Eisenbeiser *et al.*<sup>10</sup> have fabricated a transistor that behaves comparably to a 8-Å-thick SiO<sub>2</sub>/Si MOSFET. The improvement in transistor

TABLE I. Reference configuration and cutoff radii (in bohr) of the pseudopotentials used in our study. Because of the inclusion of the semicore states in valence and within the Troullier-Martin scheme, Ba, Ti, and Sr pseudopotentials must be generated for ionic configurations (ionic charge +2). However, these are more suitable than the neutral ones, given the oxidation numbers of these atoms in the alkaline-earth oxides and perovskites.

| Reference          |          | Ba<br>$5s^2, 5p^6, 5d^0, 4f^0$ | Sr<br>$4s^2, 4p^6, 4d^0, 4f^0$ | Ti<br>$3s^2, 3p^6, 3d^2, 4f^0$ | O<br>$2s^2, 2p^4, 3d^0, 4f^0$ |
|--------------------|----------|--------------------------------|--------------------------------|--------------------------------|-------------------------------|
| Core radius (a.u.) | <i>s</i> | 1.75                           | 1.50                           | 1.30                           | 1.15                          |
|                    | <i>p</i> | 2.00                           | 1.50                           | 1.30                           | 1.15                          |
|                    | <i>d</i> | 2.50                           | 2.00                           | 1.30                           | 1.15                          |
|                    | <i>f</i> | 2.50                           | 2.00                           | 2.00                           | 1.50                          |

performance was very satisfactory, and the leakage currents was two order of magnitudes smaller than in a similar SiO<sub>2</sub>-based device.

As was pointed out before, the barrier height of the dielectric with respect to the Si substrate should be large enough to minimize carrier injection into the conduction-band states. A large value of the conduction-band offset (CBO) between Si and the gate dielectric is required, and typically materials with CBO smaller than 1.0 eV are rejected for further applications. Robertson and Chen,<sup>11</sup> aligning the charge neutrality levels<sup>12</sup> (CNL's) of both semiconductors, have estimated the CBO for a Si/SrTiO<sub>3</sub> interface to  $-0.14$  eV (SrTiO<sub>3</sub> below—that is, no barrier at all for the electrons) in very good agreement with experimental results.<sup>13</sup> This prevents, in principle, the use of titanate as the gate dielectric in electronic devices. However, the presence of the buffer alkaline-earth oxide in the heterostructure was missing in their approach. In this paper, we will show that in addition to providing a physical separation between Si and the perovskite, the presence of the alkaline-earth oxide also allows one to monitor efficiently the band offset.

We report a study of the properties of BaO/BaTiO<sub>3</sub> (from now on, we will refer to this heterostructure as the Ba interface) and SrO/SrTiO<sub>3</sub> (Sr-interface) structures from first principles. The method on which the simulations are based is described in Sec. II. In Sec. III, we discuss the details of the atomic structure at the interfaces. The electronic structure is presented in Sec. IV, where we analyze the density of states at the junctions. In Sec. V, we study the band offset at the interface. Finally, in Sec. VI, an estimate of the band alignment of the whole Si/SrO/SrTiO<sub>3</sub>/Pt and Si/BaO/BaTiO<sub>3</sub>/SrRuO<sub>3</sub> structures will be given.

## II. TECHNICALITIES

Our calculations have been performed within density-functional theory<sup>14</sup> (DFT) and the local density approximation<sup>15</sup> (LDA). We used a numerical atomic orbital (NAO) method, as it is implemented in the SIESTA code.<sup>16–18</sup> The exchange-correlation functional was approximated using Perdew-Zunger<sup>19</sup> parametrization of Ceperley-Alder data.<sup>20</sup>

Core electrons were replaced by *ab initio* norm-conserving fully separable<sup>21</sup> Troullier-Martin<sup>22</sup> pseudopotentials. Due to the large overlap between the semicore and

valence states, the  $3s$  and  $3p$  electrons of Ti,  $4s$  and  $4p$  electrons of Sr, and  $5s$  and  $5p$  electrons of Ba were explicitly included in the calculation. Ti, Sr, and Ba pseudopotentials were generated scalar relativistically. The reference configuration and cutoff radii for all the atoms we used are shown in Table I.

The one-electron Kohn-Sham eigenstates were expanded in a basis of strictly localized<sup>23</sup> numerical atomic orbitals.<sup>24</sup> Basis functions were obtained by finding the eigenfunctions of the isolated atoms confined within the new soft-confinement spherical potential proposed in Ref. 25. We used a single- $\zeta$  basis set for the semicore states of Ti, Sr, and Ba and double- $\zeta$  plus polarization for the valence states of all the atoms. For Sr (Ba) an extra shell of  $4d(5d)$  orbitals was added. All the parameters that define the shape and the range of the basis functions for Ba, Ti, and O were obtained by a variational optimization in cubic bulk BaTiO<sub>3</sub>, following the procedure described in Ref. 25. For Sr, another optimization was performed in bulk SrTiO<sub>3</sub>, frozen in the atomic orbitals of Ti and O to these previously optimized in BaTiO<sub>3</sub>.<sup>26</sup>

The electronic density, Hartree, and exchange-correlation potentials, as well as the corresponding matrix elements between the basis orbitals, were calculated in a uniform real-space grid.<sup>16</sup> An equivalent plane-wave cutoff of 200 Ry was used to represent the charge density. Once self-consistency was reached, the grid was refined (reducing the distance between grid points by half) to compute the total energy, atomic forces, and stress tensor.

The integrals in reciprocal space were well converged, using in all the cases a sampling in  $\vec{k}$  of the same quality as the  $(6 \times 6 \times 6)$  Monkhorst-Pack<sup>27</sup> mesh in bulk BaTiO<sub>3</sub>. The equivalent cutoff length<sup>28</sup> for this sampling,  $13 \text{ \AA}$ , was the one employed in all simulations. This represents a large number of  $\vec{k}$  points thought that all the materials involved in the heterojunctions are insulators. However, it has been proved that this fineness is mandatory while dealing with perovskites.<sup>29</sup>

Tests of the performance of the SIESTA method on perovskites were done in bulk BaTiO<sub>3</sub>.<sup>30</sup> Lattice constants, ferroelectric distortions, Born effective charges, and phonon dispersion curves are in very good agreement with plane waves<sup>29,31–33</sup> and full-potential linear augmented plane-wave (FP-LAPW) calculations.<sup>34</sup>

TABLE II. Experimental and theoretical lattice constants ( $a$ , in Å) for the different compounds involved in our heterostructures. The lattice mismatch  $f$  between a given epilayer and the Si substrate (in % with respect to the substrate lattice constant) is also reported.  $d_{A-A}$  ( $A = \text{Ba}$  or  $\text{Sr}$ ), stands for  $A$ - $A$  nearest-neighbor distance in  $A$  O oxides. Perovskite values refer to the cubic structure.

| System             | Experimental              |         | LDA-DFT                    |         |
|--------------------|---------------------------|---------|----------------------------|---------|
|                    | $a$ (Å)                   | $f$ (%) | $a$ (Å)                    | $f$ (%) |
| Si                 | 5.43 <sup>a</sup>         |         | 5.389 <sup>b</sup>         |         |
| BaO                | 5.52 <sup>a</sup>         | 1.66    | 5.433                      | 0.82    |
|                    | $(d_{\text{Ba-Ba}}=3.90)$ |         | $(d_{\text{Ba-Ba}}=3.842)$ |         |
| BaTiO <sub>3</sub> | 4.00 <sup>c</sup>         | 4.18    | 3.948                      | 3.60    |
| Si                 | 5.43 <sup>a</sup>         |         | 5.389 <sup>b</sup>         |         |
| SrO                | 5.16 <sup>a</sup>         | -4.97   | 5.075                      | -5.83   |
|                    | $(d_{\text{Sr-Sr}}=3.65)$ |         | $(d_{\text{Sr-Sr}}=3.588)$ |         |
| SrTiO <sub>3</sub> | 3.91 <sup>d</sup>         | 1.83    | 3.874                      | 0.90    |

<sup>a</sup>Reference 35.

<sup>c</sup>Reference 36.

<sup>b</sup>Reference 16.

<sup>d</sup>Reference 37.

### III. ATOMIC STRUCTURE AT THE INTERFACE

In Table II we report the experimental and calculated lattice parameters of the different materials involved in our heterostructures, together with the lattice mismatch with respect to the Si substrate. The misfit is defined as  $f = 100 \times (a - a_{\text{Si}})/a_{\text{Si}}$ , where  $a$  and  $a_{\text{Si}}$  are, respectively, the lattice constant of the epilayer and Si. The value of  $f$  is positive when the epilayer is compressed and negative when it is expanded. In Table II, we observe that the LDA produces a systematic underestimate of the lattice constant (about 1%). Nevertheless, the correct sequence of lattice mismatch is obtained so that the calculations will reproduce the experimental strain conditions when working at the theoretical lattice constants of the substrate.

Interfaces were simulated using a supercell approximation. The basic unit cell, periodically repeated in space, corresponds to the generic  $(A O)_n / (A O - B O_2)_m$  formula, where  $n$  and  $m$  are, respectively, the number of  $A$  O oxide atomic planes and the number of  $AB O_3$  unit cells.<sup>7</sup> For even  $n$  and odd  $m$  (the only cases studied in this work), this structure possesses two mirror symmetry planes located on the central  $A$  O and  $B O_2$  layers.

We considered pseudomorphic heterojunctions, so that the lattice constant parallel to the plane of the interface,  $a_{\parallel}$ , is assumed to remain the same on both sides of the structure. The choice of  $a_{\parallel}$  allows us to treat implicitly the mechanical effect of the substrate, which is not included explicitly in the calculations.

To establish the notation, we will call the plane parallel to the interface the  $(x, y)$  plane, whereas the perpendicular direction will be referred to as the  $z$  axis.

Under the strain conditions imposed by the Si substrate, the epitaxial layers will minimize the elastic energy by elongation or compression of the lattice constant along  $z$ ,  $a_{\perp}$ . To determine its value, strain relaxations of the bulk unit cells of  $A$  O and  $AB O_3$  were performed under the constraint of fixed  $a_{\parallel}$ . Since the lattice misfit between the substrate and

TABLE III. Theoretical elastic constants  $c_{11}$  and  $c_{12}$  (in Mbar).

|                    | $c_{11}$ | $c_{12}$ | $2(c_{12}/c_{11})$ |
|--------------------|----------|----------|--------------------|
| BaO                | 2.10     | 0.57     | 0.54               |
| BaTiO <sub>3</sub> | 3.71     | 1.26     | 0.68               |
| SrO                | 2.36     | 0.57     | 0.48               |
| SrTiO <sub>3</sub> | 3.93     | 1.17     | 0.59               |

epilayers is small enough to remain in the linear regime, the different values of  $a_{\perp}$  with respect to the in-plane lattice constant can be predicted from the macroscopic theory of elasticity (MTE), and therefore an estimation of the atomic structure of the interface can be done. Following the description of Ref. 38 and for an interface orientation along (001),

$$a_{i,\perp} = [1 - D_i \varepsilon_{i,\parallel}] a_i,$$

$$\varepsilon_{i,\parallel} = \frac{a_{i,\parallel}}{a_i} - 1,$$

$$D_i = 2 \frac{c_{12}^i}{c_{11}^i}, \quad (1)$$

where  $a_i$ ,  $c_{11}^i$ , and  $c_{12}^i$  stand for, respectively, the equilibrium lattice parameter and the elastic constants of material  $i$ . Theoretical values of the elastic constants are reported in Table III. Bulk structures from the macroscopic theory are in excellent agreement with the first-principles results, as can be drawn from the results in Table IV (relative errors within 1% for all the cases).

The resulting bulk tetragonal unit cells were used as the building blocks of our supercell. However, as interplanar distances in the region close to the interface are not predicted

TABLE IV. Lattice constant perpendicular to the plane of the interface,  $a_{\perp}$ , at different values of the in-plane lattice constant  $a_{\parallel}$ . Results from both first-principles structural minimizations (FP's) and macroscopic theory of elasticity (MTE) are reported. Units in Å.

| System             | $a_{\parallel}$ | $a_{\perp}^{MTE}$ | $a_{\perp}^{FP}$ |
|--------------------|-----------------|-------------------|------------------|
| BaO                | 5.389           | 5.457             | 5.457            |
|                    | 5.430           | 5.435             | 5.433            |
|                    | 5.665           | 5.307             | 5.322            |
| BaTiO <sub>3</sub> | 3.811           | 4.041             | 4.054            |
|                    | 3.839           | 4.022             | 4.025            |
|                    | 4.006           | 3.909             | 3.911            |
| SrO                | 5.389           | 4.924             | 4.939            |
|                    | 5.430           | 4.905             | 4.923            |
|                    | 5.522           | 4.861             | 4.893            |
| SrTiO <sub>3</sub> | 3.811           | 3.912             | 3.915            |
|                    | 3.839           | 3.895             | 3.893            |
|                    | 3.904           | 3.856             | 3.857            |

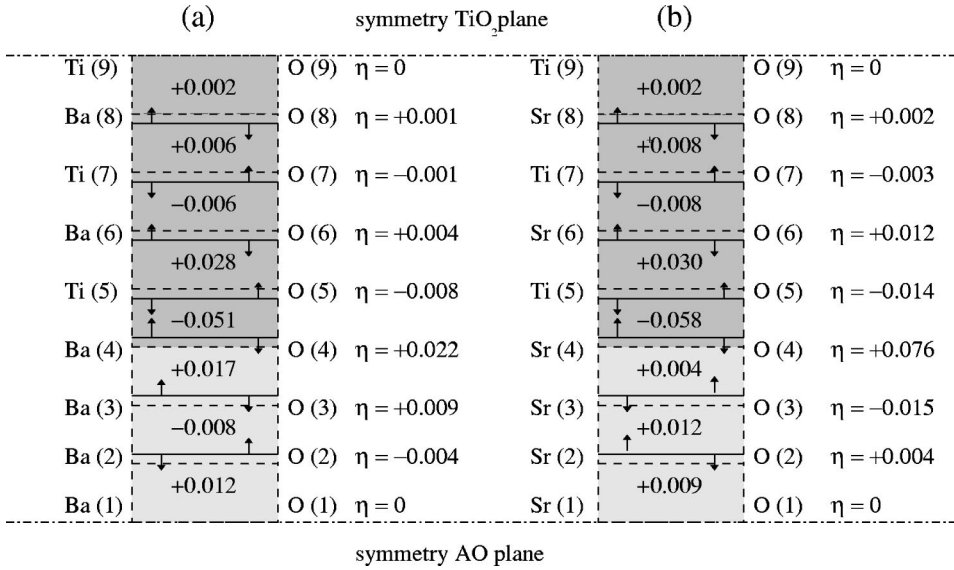


FIG. 1. Schematic view of the atomic relaxation for the bottom half of BaO/BaTiO<sub>3</sub> (a) and SrO/SrTiO<sub>3</sub> (b) supercells. Dashed lines correspond to the *reference* positions of the atomic planes, and the solid lines are the mean position in the relaxed structure. Changes in the interplanar distance are written in Å. The atoms (A or Ti, depending on the layer, at the left and O at the right) move in the direction indicated by the arrow. The rumpling parameter  $\eta$  is expressed in Å. The size of the heterostructure corresponds to  $n=6$ ,  $m=5$ .

properly from MTE,<sup>39</sup> a full relaxation of the geometry using first-principles methods was needed.

For each interface, a *reference* ionic configuration was defined by piling up truncated bulk strained materials. Atomic coordinates were then relaxed until the maximum component of the force on any atom was smaller than 10 meV/Å. The maximum component of the stress tensor along  $z$  was smaller than  $5 \times 10^{-3}$  eV/Å<sup>3</sup> for the Ba interface and smaller than  $7 \times 10^{-3}$  eV/Å<sup>3</sup> for the Sr interface. It has been confirmed that additional relaxation of  $a_{\perp}$  (neglected in this work) does not produce any significant change.

In order to characterize the atomic displacements induced by the relaxation, we define  $\delta_z(M_i)[\delta_z(O_i)]$  as the displacement of the cation [oxygen] along  $z$  at layer  $i$ , with respect to the initial *reference* configuration. We introduce the displacement of the mean position of each atomic plane as  $\beta_i = [\delta_z(M_i) + \delta_z(O_i)]/2$  and the change in the interplanar distance between consecutive planes  $i$  and  $j$  as  $\Delta d_{ij} = \beta_i - \beta_j$ . The rumpling parameter of layer  $i$  describes the movement of the ions with respect to the mean position of each atomic plane and corresponds to  $\eta_i = [\delta_z(M_i) - \delta_z(O_i)]/2$ . It is positive when the cation  $M_i$  is above the oxygen, and negative otherwise.

Figure 1 shows a schematic view of the atomic relaxations for both Ba and Sr interfaces, when the in-plane lattice constant was constrained to the theoretical one of Si. The most important features are (i) a compression of the interplanar distance at the interface layer; (ii) the appearance of an ionic interface dipole, due to the opposite motion of the anion and the cation at the A O layer closest to the interface—the anion moves towards the A O region whereas the cations displaces inside the AB O<sub>3</sub> part; (iii) a monotonic decay of the absolute value of the rumpling parameter as a function of the distance to the A O-interface layer, where the major relaxations are localized; and (iv) the oscillatory behavior of the sign of  $\eta_i$  and  $\beta_i$  inside the perovskite from layer to layer, as happens also in AB O<sub>3</sub> free-standing slabs.<sup>40,41</sup>

The main difference between the Ba and Sr heterostructures is the magnitude of the relaxations at the interface,

larger in the last case. All these conclusions are independent of the in-plane lattice constant imposed in the calculation and show very good agreement with the results obtained using the ABINIT (Ref. 42) plane-wave pseudopotential code.<sup>43</sup>

#### IV. ELECTRONIC STRUCTURE AT THE INTERFACE

In Fig. 2, we report the energy-band structure along a selected high-symmetry line in the first Brillouin zone for the bulk alkaline-earth oxides ( $\Gamma X$  line) and cubic bulk perovskite structures ( $\Gamma R$  line). Only bands close to the Fermi level are represented. The valence bands are mainly composed of O 2*p* states that, in the case of the perovskites, show significant hybridizations with Ti 3*d* orbitals.

All the alkaline-earth and perovskite oxides we consider are insulators (experimental gaps above 3 eV). Within the cubic symmetry (in the absence of strains) and neglecting spin-orbit couplings, the computed band gap for both

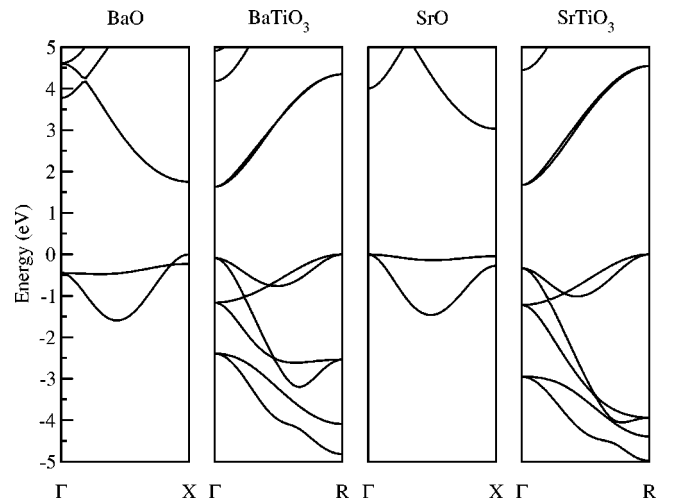


FIG. 2. Bulk band structures of cubic BaO, BaTiO<sub>3</sub>, SrO, and SrTiO<sub>3</sub> at the theoretical lattice constant. The zero of energy has been assigned to the top of the valence band in each case. Only the bands closed to the gap are plotted.

TABLE V. Theoretical ( $E_{gap}^{theo}$ ) and experimental ( $E_{gap}^{expt}$ ) band gaps in eV for the materials involved in our simulations. The theoretical value, within the LDA, has been calculated at the theoretical lattice constant.

|                  | BaO              | BaTiO <sub>3</sub> | SrO              | SrTiO <sub>3</sub> |
|------------------|------------------|--------------------|------------------|--------------------|
| $E_{gap}^{theo}$ | 1.75             | 1.63               | 3.03             | 1.67               |
| $E_{gap}^{expt}$ | 4.8 <sup>a</sup> | 3.2 <sup>b</sup>   | 5.7 <sup>a</sup> | 3.3 <sup>c</sup>   |

<sup>a</sup>Reference 44.

<sup>b</sup>Reference 45.

<sup>c</sup>Reference 7.

BaTiO<sub>3</sub> and SrTiO<sub>3</sub> is indirect ( $R \rightarrow \Gamma$ ). The topmost valence and the bottom most conduction bands are 3 times degenerated at these high-symmetry points. Under the same conditions, the gap is also indirect in SrO, with three degenerated uppermost valence bands at  $\Gamma$  and a single lowest conduction band at  $X$ , whereas BaO exhibits a direct gap, between single bands at  $X$ .

In Table V we report experimental and theoretical bands gaps (within the LDA) for all materials involved in our study. We see that, due to the well-known DFT “band-gap problem,” the theoretical values are underestimated by about 50% in each case. Nevertheless, it is usually accepted that this error can be roughly compensated by an appropriate shift of the conduction bands which should not affect the conclusions of the character of the gap reported in this section.

A uniaxial strain along (001) lowers the symmetry of the perovskites from  $Pm3m$  to  $P4mm$ . This translates into a splitting of the top of the valence bands into a singlet and a doublet. The singlet is above (below) for a compressive (tensile) strain. For the alkaline-earth oxides, the symmetry reduces from  $Fm\bar{3}m$  to  $I4/mmm$ . The top of the valence band of SrO is therefore split but, in this case, the doublet is above (below) the singlet for a compressive (tensile) strain. Spin-orbit couplings (not considered in this work) might introduce further splittings.

Figure 3 shows the projected density of states (PDOS) on the different atoms (sum of the projections of the DOS on all the atomic orbitals of the given atom) as a function of the depth of the layer inside the material for the BaO/BaTiO<sub>3</sub> and SrO/SrTiO<sub>3</sub> interfaces. The main conclusions that can be extracted are as follows: (i) the absence of any interface induced gap states clearly demonstrates the semiconductor character of the heterostructures; (ii) the features of the PDOS on the alkaline-earth and the O atom at the interface layer (labeled as 4) are much closer to the ones displayed in bulk  $ABO_3$  than in bulk  $AO$ , showing a dominant  $ABO_3$  character of the interface; (iii) the PDOS converges very quickly to the bulk properties, and many of the bulk features can be recovered even at the atomic layers closest to the interface; and (iv) atomic relaxations have small effects on the shape of the PDOS, as can be seen comparing the solid and dotted curves in the figure. Only a shift in the SrO layers towards zero energy (chosen as the top of the valence band in each case) is noticeable. This effect is a direct consequence of the relaxation-induced interface dipole discussed in Sec. III. The different magnitude of the dipole between the

Ba and Sr interfaces explains why the shift is almost negligible in the Ba heterostructure.

## V. BAND OFFSETS

One of the most important physical quantities that characterize the interface between semiconductors or insulators is the band offset, i.e., the relative position of the energy levels on both sides of the interface. The valence-band offset (VBO) [conduction-band offset (CBO)] is defined as the difference between the positions of the top of the valence bands [the bottom of the conduction bands] of the two materials. These band discontinuities play a fundamental role in calculating the transport properties through heterojunction devices.

The determination of these offsets from first principles cannot be achieved from a direct comparison of the corresponding band edges in the two compounds as obtained from two independent bulk band-structure calculations. The reason is the lack of an intrinsic energy scale to refer all the energies: in a first-principles simulation, the Hamiltonian eigenvalues are referred to an average of the electrostatic potential that is ill defined for infinite systems<sup>46</sup> (it is only defined to within an arbitrary constant). Consequently, together with the eigenvalue difference, we must consider the lineup of this average between the two materials. This potential shift depends on the dipole induced by the electronic charge transferred from one part of the interface to the other after the interfacial hybridization (the electronic charge density of each system will decay into the other in an, in principle, unknown way). As the transfer of charge depends not only on the materials that constitute the interface, but also on the particular orientation, the lineup can only be obtained from a self-consistent calculation on a supercell including both materials.

Therefore, from a theoretical point of view, the band offsets are usually split into two terms:<sup>47,48</sup>

$$\begin{aligned} \text{VBO} &= \Delta E_v + \Delta V \\ \text{CBO} &= \Delta E_c + \Delta V. \end{aligned} \quad (2)$$

The first contribution  $\Delta E_v$  ( $\Delta E_c$ ) is referred to as the *band-structure term*. It is defined as the difference between the top (bottom) of the valence (conduction) bands as obtained from two independent standard bulk band-structure calculations at the same strained geometries as in the supercell construction. Within the LDA, only a first estimate of the band-structure term can be obtained,  $\Delta E_{v,c}^{LDA}$ . To get more accurate results, a correction dealing with many-body effects in the quasiparticle spectra should be added:

$$\Delta E_{v,c} = \Delta E_{v,c}^{LDA} + \Delta E_{v,c}^{corr}. \quad (3)$$

Self-energy corrections are often obtained within the GW approximation.<sup>49</sup> They strongly modify the description of the conduction bands and tend to solve the “band-gap problem” mentioned in Sec. IV. Even the valence-band energies might be subject to certain errors, especially in oxides.<sup>50</sup> Unfortunately, no accurate GW data are currently available for  $AO$  and  $ABO_3$  compounds. Only model GW calculations have been performed recently for SrO and SrTiO<sub>3</sub> and with lim-

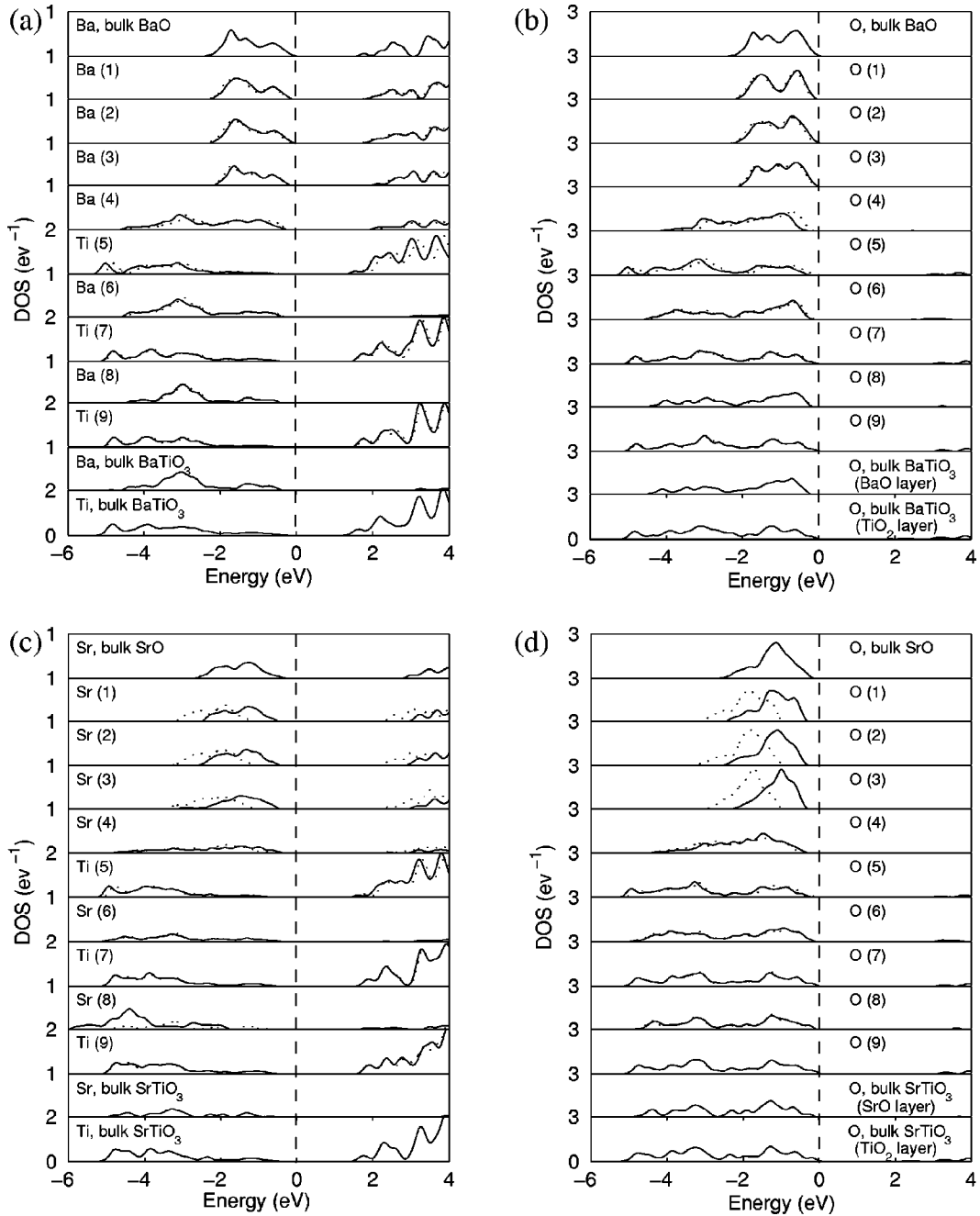


FIG. 3. Projected density of states on all the atoms as a function of the distance to the interface for the BaO/BaTiO<sub>3</sub> (a) and (b) and SrO/SrTiO<sub>3</sub> (c) and (d) heterostructures. Solid lines represent the projection for the relaxed geometry and dotted lines for unrelaxed coordinates. Atomic layers are identified as in Fig. 1. Projected densities of states of bulk A O and AB O<sub>3</sub> are also plotted for comparison. All the energies have been rigidly displaced in order to align the top of the valence band (vertical line) with zero. The imposed  $a_{\parallel}$  was set up to the theoretical one of Si (5.389 Å).

ited success.<sup>51</sup> To overcome the problem, we make the approximation that the errors in the valence bands are smaller than those for the conduction bands and of the same order of magnitude for the two compounds taking part in the heterostructures so that they tend to cancel each other ( $\Delta E_v^{corr} = 0$ ). Knowing the relative position of the valence bands, we simply add the experimental band gaps (see Table V) to obtain the discontinuities for the conduction bands [ $\Delta E_c = \Delta E_v^{LDA} + \Delta E_{gap}^{expt}$ , where  $\Delta E_{gap}^{expt}$  is defined as  $E_{gap}^{expt}(B) - E_{gap}^{expt}(A)$  at a junction A/B].

The second term  $\Delta V$  is the *lineup of the average of the electrostatic potential* through the heterojunction. This macroscopic quantity summarizes all the intrinsic interface effects, such as the chemical composition, structural details, and orientation. To obtain it, we start from the total (ionic plus electronic) microscopic electrostatic Hartree potential, output of the self-consistent supercell calculation (we refer the reader to the Appendix for a detailed explanation about the relationship between the zero-energy level and the average of the electrostatic potential). Then, we apply the double-

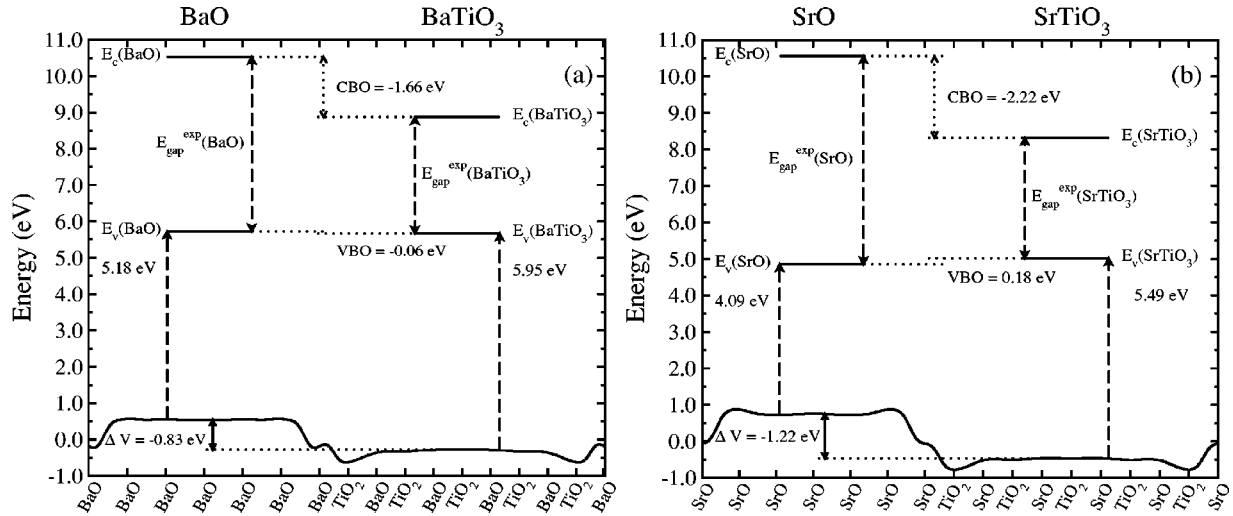


FIG. 4. Schematic representation of the valence-band offset (VBO) and the conduction-band offset (CBO) for BaO/BaTiO<sub>3</sub> (a) and SrO/SrTiO<sub>3</sub> (b) interfaces.  $E_v$ ,  $E_c$ , and  $E_{gap}^{exp}$  stand for the top of the valence band, the bottom of the conduction band, and the experimental band gap, respectively. Values for  $E_v$ , measured with respect to the average of the electrostatic potential in each material, are indicated. The solid curve represents the profile of the macroscopic average of the total electrostatic potential across the interface.  $\Delta V$  stands for the resulting lineup. The in-plane lattice constant was set up to the theoretical one of Si (5.389 Å). The size of the supercell corresponds to  $n = 6$  and  $m = 5$ .

macroscopic average<sup>47,48,52</sup> technique. It consists of performing first the average of the electrostatic potential over planes parallel to the interface and then averaging the obtained quasiperiodic one-dimensional function with two steplike filter functions whose lengths  $l_1$  and  $l_2$  are determined by the periodicity of the constituents. Here  $l_1$  and  $l_2$  have been set up to the distance between equivalent A O and TiO<sub>2</sub> planes in the alkaline-earth oxide and in the perovskite, respectively. A full description of the method to the A O/ABO<sub>3</sub> heterostructures can be found in Ref. 53. The resulting profile of the macroscopic potential is flat on both sides far enough from the interface (*bulklike regions*).  $\Delta V$  is defined as the difference between these two plateau values (see Fig. 4). The lineup should be independent of the length used in the filter functions. We have checked that doubling the size of the steplike functions introduces a numerical uncertainty in  $\Delta V$  of the order of 30 meV. This is the main source of inaccuracy in our calculations of the band offsets.<sup>48</sup>

It is worth noticing that neither  $\Delta E_v$  nor  $\Delta V$  has any physical meaning of its own, being pseudopotential-dependent numbers. Only the sum of both is physically significant and quite independent of the choice of pseudopotential.<sup>48</sup>

### First-principles results

Figure 4 shows a schematic representation of the band-structure discontinuities for the BaO/BaTiO<sub>3</sub> and SrO/SrTiO<sub>3</sub> heterostructures, both of them calculated fixing the in-plane lattice constant at the theoretical one of Si. Band splittings stemming from strain are taken into account in the figure. We use the same sign convention as Van de Walle and Martin:<sup>54</sup> a positive value of the band offset for the discontinuity at a junction A/B corresponds to an upward step in going from A to B.

From the figure, we conclude that the Ba interface is type II, with both the valence and conduction bands of BaTiO<sub>3</sub> falling in energy below the corresponding ones of BaO. Within the accuracy of our calculations, BaO and BaTiO<sub>3</sub> topmost valence bands are almost aligned (an offset of only  $-0.06$  eV is predicted), so the barrier in the conduction bands is mainly due to the difference in the band gaps of both materials and, inferred from the experimental values, amounts to  $-1.66$  eV.

The Sr interface is type I, meaning that the band gap of SrTiO<sub>3</sub> lies completely inside the gap of SrO. An upward step of  $+0.18$  eV for the valence bands is theoretically expected, which implies a CBO of  $-2.22$  eV.

A rough estimate of the valence-band offset was already accessible<sup>55</sup> by identifying in Fig. 3 the position of the top of the valence band in the PDOS for the O atom at both symmetry planes, in the bulklike regions of the materials that constitute the interface (numbered as 1 for A O and 9 for AB O<sub>3</sub>). The values deduced from the figure are  $-0.09$  eV for the Ba interface (BaO above) and  $+0.28$  eV for the Sr interface (SrTiO<sub>3</sub> above), close to those obtained using the macroscopic average technique. However, these numbers must be taken with care:<sup>48</sup> this method to compute band offsets requires calculations with a higher number of special  $\vec{k}$  points than those needed to converge the charge density or the potential lineup.

It is important to note here the *crucial* role played by the atomic relaxations at these interfaces. As was pointed out in Sec III, after the relaxation process an extra dipole appears at the junction that modifies the electrostatic lineup across the interface<sup>56</sup> and, consequently, the band offsets:

$$\delta(\Delta V) = \frac{4\pi}{a_{\parallel}^2} \sum_{\kappa\alpha} \frac{Z_{\kappa,\alpha z}^{*(T)}}{\epsilon_{\infty}} \Delta u_{\kappa\alpha}, \quad (4)$$

TABLE VI. Valence-band offsets (VBO's) for BaO/BaTiO<sub>3</sub> and SrO/SrTiO<sub>3</sub> interfaces. Values are reported at different in-plane lattice constants  $a_{\parallel}$ . Here  $\Delta E_v$  and  $\Delta V$  stand for, respectively, the band-structure term and the lineup of the electrostatic potential contributions to the VBO's. The size of the heterostructures corresponds to  $n=6$ ,  $m=5$ .

| $a_{\parallel}$ (Å) | BaO/BaTiO <sub>3</sub> |        |        |        | SrO/SrTiO <sub>3</sub> |        |        |
|---------------------|------------------------|--------|--------|--------|------------------------|--------|--------|
|                     | 5.389                  | 5.430  | 5.583  | 5.665  | 5.389                  | 5.430  | 5.522  |
| $\Delta V$          | -0.834                 | -0.833 | -0.746 | -0.755 | -1.217                 | -1.190 | -1.128 |
| $\Delta E_v$        | 0.772                  | 0.807  | 0.600  | 0.560  | 1.401                  | 1.340  | 1.209  |
| VBO                 | -0.062                 | -0.026 | -0.146 | -0.195 | 0.184                  | 0.150  | 0.081  |

where  $\delta(\Delta V)$  is the change in the electrostatic lineup along the  $z$  direction due to the atomic displacements,  $Z_{\kappa,\alpha\beta}^{*(T)}$  is the Born effective tensor of atom  $\kappa$ ,  $\Delta u_{\kappa\alpha}$  its displacement along the Cartesian direction  $\alpha$  during the relaxation, and  $\epsilon_{\infty}$  the optical dielectric constant. Looking at the magnitude of the atomic displacements, it is reasonable that the change should be more remarkable for the Sr interface than for the Ba one. From our *ab initio* calculations and for the same supercell used to get results in Fig. 4, we observe a change in  $\Delta V$  of  $-0.67$  eV for the Sr interface (from  $-0.55$  eV for the unrelaxed geometry to  $-1.22$  eV after the relaxation), whereas in the Ba interface the deviation amounts to  $-0.11$  eV (from  $-0.72$  eV to  $-0.83$  eV). This emphasizes the importance of performing accurate first-principles atomic relaxations for correct predictions of the barriers.

To what extent do these discontinuities change with the in-plane lattice constant? This is an important question because a dependence with strain would allow us to tune the band offsets [for example, replacing the Si substrate by Ge (Ref. 7) in order to impose a different lattice parameter throughout the interface] depending on the required values for a given device. In order to check this point, we have carried out calculations at different in-plane lattice constants. For all the different strain conditions both the supercell length and the atomic coordinates were relaxed as explained in Sec. III. In Table VI and Fig. 5 we summarize the results for both Ba and Sr heterostructures. In both cases a variation by about 0.1 eV in VBO's with the in-plane lattice constant is observed, mainly due to the band-structure term (a consequence of the strain-induced splittings of the top valence-band manifold), as happens for other lattice-mismatched, isovalent, common anion interfaces.<sup>57</sup> The change is almost linear and tends to lower the energy of the valence bands of the  $ABO_3$  perovskite with respect to the  $AO$  alkaline-earth oxide.

The band-structure term displays a linear behavior with strain for the Sr interface [see Fig. 5(a)]. The anomalous behavior of  $\Delta E_v$  for the Ba interface is due to a modification in the character of the top of the valence band of BaO under strain. It changes from  $X$  when BaO is compressed to  $Z$  when it is expanded. This transformation occurs for a lattice constant around  $5.43$  Å (theoretical lattice parameter of BaO). In Fig. 5(a) we plot the difference between the top of the valence band of BaTiO<sub>3</sub> and the highest occupied state at  $X$  and  $Z$  of BaO. The crossing point is clearly identified in the figure. No extra changes in the linear behavior of  $\Delta E_v$  are expected for longer lattice constants.

The almost-linear change in the lineup term can be explained according to an analytic scaling law proposed in Ref. 58. Once  $\Delta V$  is known for a reference configuration with an in-plane lattice constant  $a_{\parallel}$ , then, supposing a uniform strain throughout the structure,  $\Delta V'$  for any other strained configuration  $a'_{\parallel}$  can be extrapolated from

$$\Delta V' \approx \frac{1}{(1 + \epsilon_{\parallel})^2} \Delta V, \quad (5)$$

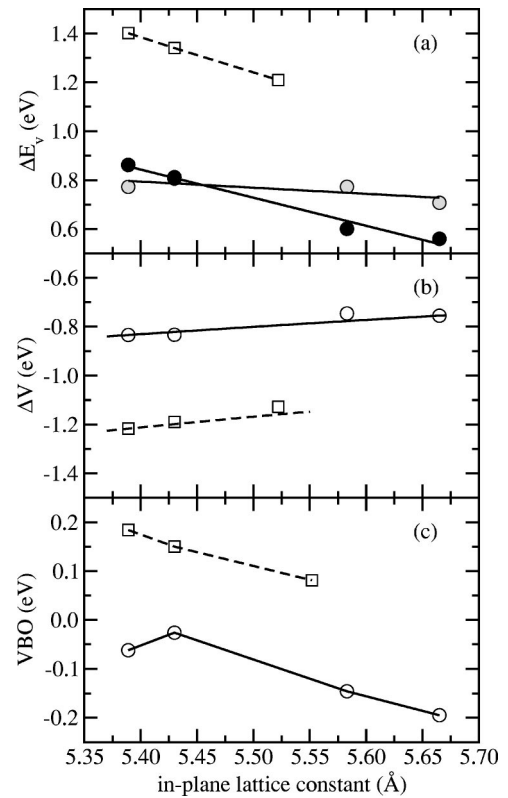


FIG. 5. Dependence with in-plane strain of the valence-band offset (VBO) and of its decomposition into the band-structure ( $\Delta E_v$ ), and lineup ( $\Delta V$ ) terms. Squares and circles represent, respectively, the first-principles results for the SrO/SrTiO<sub>3</sub> and BaO/BaTiO<sub>3</sub> interfaces. In (a), gray-filled (black-filled) circles stand for the difference between the top of the valence band of BaTiO<sub>3</sub> and the highest occupied state at  $X$  ( $Z$ ) point in BaO. Lines in (a) and (c) (dashed for Sr and solid for the Ba interface) are a guide to the eye. Lines in (b) represent the results of the analytic scaling law proposed in Ref. 58.



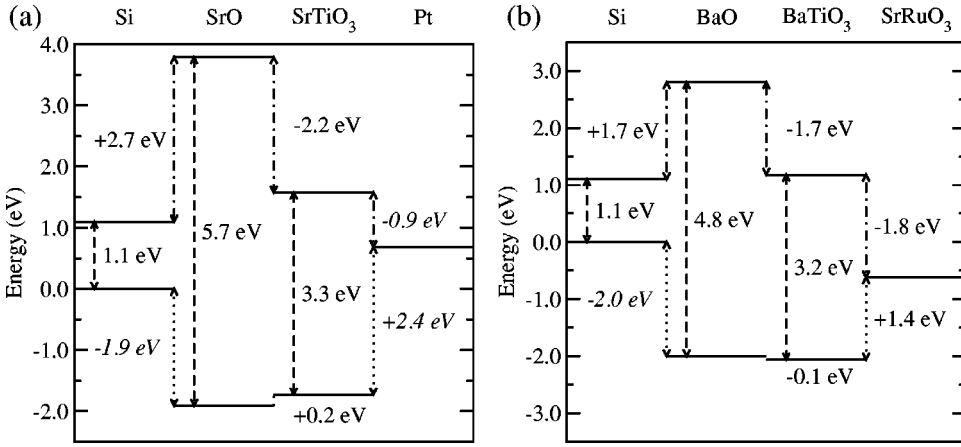


FIG. 6. Estimation of the valence (dotted lines) and conduction (dot-dashed lines) band offsets for the whole heterostructures Si/SrO/SrTiO<sub>3</sub>/Pt (a) and Si/BaO/BaTiO<sub>3</sub>/SrRuO<sub>3</sub> (b). Dashed lines represent the experimental band gaps. Theoretical value for the VBO between Si and A O (in italic) has been taken from Ref. 59 for the Sr interface and from Ref. 60 for the Ba interface. Theoretical Schottky barriers between SrTiO<sub>3</sub> and Pt (also in italic) have been taken from Ref. 11.

where  $\varepsilon_{\parallel} = (a_{\parallel}'/a_{\parallel} - 1)$ . Figure 5(b) shows a comparison of the first-principles and extrapolated values, where the heterostructure at the in-plane lattice constant of Si has been chosen as the reference configuration. Results are in good agreement within the numerical accuracy of the *ab initio* simulations.

In summary, the VBO varies almost linearly for a large range of in-plane strains. The only deviation is observed for BaO/BaTiO<sub>3</sub> and is explained by a change of character of the BaO gap under compression.

## VI. INTERFACE WITH Si

As was pointed out in the Introduction, the A O/AB O<sub>3</sub> interface is only a part of the gate stack of technological interest for the semiconductor industry. A O acts as a buffer layer between the Si substrate and the high- $\kappa$  perovskite. The whole heterostructure epitaxially grown following the McKee-Walker process<sup>8</sup> is made of Si/ASi<sub>2</sub>/A O/AB O<sub>3</sub>.<sup>6</sup> As will be emphasized in this section, the role of the buffer layer is not only the passivation of the Si substrate, but also the efficient tuning of the offsets between the perovskite and the channel.

Combining our results with various data available in the literature, we can estimate the band discontinuities along the whole heterostructures of technological interest as summarized in Fig. 6. Previous theoretical calculations of the band offsets between the alkaline-earth oxide A O and Si have been reported recently [Si/BaO (Ref. 60) and Si/SrO (Ref. 59)]. In addition, we can find in the literature theoretical estimations for the Schottky barriers between perovskites and prototypical metallic electrodes [SrTiO<sub>3</sub>/Pt (Ref. 11) or BaTiO<sub>3</sub>/SrRuO<sub>3</sub> (Ref. 61)].

We must notice that, although most of the previous works (except Ref. 11) have been done using the same basic approaches (DFT, pseudopotentials,  $\vec{k}$ -point samplings, supercells, etc.), they differ in the details of the calculations (for example, they have been carried out at different in-plane lattice constants, and the size of the supercells or the parameters used to generate the pseudopotentials might change from one to the other). So only a rough estimate of the barriers can be deduced from the comparison and any quantitative conclusion is beyond the scope of this section.

Within the LDA, plus GW corrections, Bongiorno-Nardelli *et al.*<sup>59</sup> investigated the structural and electronic properties of the Si/SrSi<sub>2</sub>/SrO interface. They predicted a VBO between Si and SrO of  $-1.91$  eV for the most stable interface configuration. Using the experimental gaps to locate the conduction bands, it translates to a CBO of  $2.69$  eV. The Schottky barrier  $\phi_n$  (difference between the Fermi level and the bottom of the conduction band) between SrTiO<sub>3</sub> and Pt has been evaluated<sup>11</sup> to  $-0.89$  eV, which implies a barrier height  $\phi_p$  (difference between the Fermi level and the top of the valence band) of  $2.41$  eV. These results are summarized in the first panel of Fig. 6.

Through first-principles gradient-density-functional calculations Gulleri and Fiorentini<sup>60</sup> focused on the structure, energetic, and band offsets of the Si/BaO interface. For the favored geometry, they obtained a VBO of  $-2.0$  eV. Some of us evaluated the Schottky barriers between BaTiO<sub>3</sub> and SrRuO<sub>3</sub> (a typical metallic electrode in ferroelectric devices<sup>62</sup>) to be equal to  $\phi_p = +1.44$  eV and  $\phi_n = -1.76$  eV. These results are summarized in the second panel of Fig. 6.

For both stacks, we clearly see that the problem of the large carrier injection [expected for the perovskite in direct contact with Si (Ref. 11)] is overcome by the use of the A O layer. The electrostatic barriers for both the electrons and holes between the gate electrode and the channel are large enough to prevent carrier injections and to push the use of AB O<sub>3</sub> perovskites to a prominent position to replace silica as the gate dielectric oxide in MOSFET's.

Although the band offset is a magnitude dependent on the specific details of the interface (through the lineup term  $\Delta V$  that accounts for charge transfers and interface-dipole formation), for systems in which the charge density can be decomposed into localized atomic-charge distributions, the following transitivity rule might sometimes be satisfied:<sup>48</sup>

$$\text{VBO}(A/B) + \text{VBO}(B/C) = \text{VBO}(A/C). \quad (6)$$

As we are dealing with interfaces including rather ionic materials (like the alkaline-earth oxides), they might follow the previous rule to some extent. From Fig. 6, the extrapolations of the VBO and CBO for the direct Si/SrTiO<sub>3</sub> (Si/BaTiO<sub>3</sub>) interface are  $-1.7$  eV and  $+0.5$  eV

( $-2.1$  eV and  $0.0$  eV), in good qualitative agreement with previous experimental<sup>13</sup> and theoretical<sup>11</sup> results for Si/SrTiO<sub>3</sub>, where the barriers were found to be of around  $-2.1$  eV and  $0.0$  eV.

In other words, thanks to their wide band gap (with respect to the perovskite), the inclusion of the alkaline-earth oxide layer guarantees the existence of sufficiently high electrostatic barriers (VBO and CBO  $> 1$  eV) but does not affect the relative position of Si and  $AB$  O<sub>3</sub> electronic levels. This fact might allow us to make some guess for the alignment between the buffer layer and the perovskite oxide from the knowledge of the offsets between each material and the Si substrate.

## VII. CONCLUSIONS

We have studied structural and electronic properties of BaO/BaTiO<sub>3</sub> and SrO/SrTiO<sub>3</sub> interfaces from first principles. Atomic relaxations have been performed. Interface dipoles, due to the opposite motion of the anion and cation atoms at the interface, appear for both heterostructures. No interface electronic states are induced in the band gap. The character of the  $A$  O layer at the interface is mainly perovskite like. Under the experimental strain conditions, the valence bands of BaO and BaTiO<sub>3</sub> are almost aligned (within the accuracy of our calculations), whereas a slightly larger barrier is predicted for SrO/SrTiO<sub>3</sub>. Interface dipoles, induced by atomic relaxations, have a strong effect on the band alignments at the interface. A nearly linear variation of the VBO with in-plane strain is observed.

Gathering together our results and various data available in the literature, we make some predictions on the band alignment of whole Si/SrO/SrTiO<sub>3</sub>/Pt and Si/BaO/BaTiO<sub>3</sub>/SrRuO<sub>3</sub> structures. In both cases large enough electrostatic barriers for electrons and holes between the gate electrode and the channel are estimated, preventing the injection of carriers and suggesting that both perovskites compounds are promising candidates to replace silica in MOSFET's.

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## APPENDIX: ZERO-ENERGY REFERENCE IN SIESTA

As is mentioned in Sec. V, in all DFT first-principles codes, the Hamiltonian eigenvalues are referred to an average of the electrostatic potential that, due to the long-range character of the Coulomb interaction, is ill defined (completely arbitrary) for infinite systems.<sup>46</sup> Let us call  $V_{i+e}^H(\vec{r})$  the total (ionic + electronic) Hartree potential at a given point  $\vec{r}$  in real space. The long-range ionic contributions to the Hartree potential are included through the local part of the pseudopotential,  $V_I^{local}(\vec{r})$  ( $I$  is an atomic index), so

$$V_{i+e}^H(\vec{r}) = \sum_I V_I^{local}(\vec{r}) + V_{el}^H(\vec{r}), \quad (A1)$$

where  $V_{el}^H(\vec{r})$  is the electrostatic Hartree potential generated by the electronic charge density  $\rho^{el}(\vec{r})$ . Within the SIESTA methodology,<sup>16</sup> this last density is split into two contributions:

$$\rho^{el}(\vec{r}) = \rho^{atom}(\vec{r}) + \delta\rho(\vec{r}), \quad (A2)$$

where  $\rho^{atom}(\vec{r})$  is the sum of atomic electron charge densities  $\rho_I^{atom}(\vec{r})$  constructed by populating the basis functions with appropriate valence charges ( $\rho^{atom} = \sum_I \rho_I^{atom}$ ) and  $\delta\rho(\vec{r})$  is the deformation charge density induced by bond formation. Let  $V_I^{atom}(\vec{r})$  and  $\delta V^H(\vec{r})$  be the electrostatic potentials generated by these charge distributions. Then,

$$\begin{aligned} V_{i+e}^H(\vec{r}) &= \sum_I V_I^{local}(\vec{r}) + V_{el}^H(\vec{r}) \\ &= \sum_I V_I^{local}(\vec{r}) + \sum_I V_I^{atom}(\vec{r}) + \delta V^H(\vec{r}) \\ &= \sum_I [V_I^{local}(\vec{r}) + V_I^{atom}(\vec{r})] + \delta V^H(\vec{r}) \\ &= \sum_I V_I^{NA}(\vec{r}) + \delta V^H(\vec{r}), \end{aligned} \quad (A3)$$

where the screened neutral-atom (NA) potential, has been defined as  $V_I^{NA}(\vec{r}) \equiv V_I^{local}(\vec{r}) + V_I^{atom}(\vec{r})$ . Since the reference of  $V_I^{local}$  and  $V_I^{atom}$  is the same (both of them tend asymptotically to zero at infinite distance, as in the isolate atom) and the basis orbitals are strictly localized (they are zero beyond a given cutoff radius),  $V_I^{NA}(\vec{r})$  will vanish also beyond that range.

Averaging the total Hartree potential,

$$\langle V_{i+e}^H \rangle = \left\langle \sum_I V_I^{NA} + \delta V^H \right\rangle = \langle V^{NA} \rangle + \langle \delta V^H \rangle, \quad (A4)$$

where  $V^{NA} = \sum_I V_I^{NA}$ .

In contrast with typical plane-wave DFT codes,<sup>42</sup> where the average of  $V_{i+e}^H$  is chosen as the reference, SIESTA assigns the zero-energy level to the mean value over the unit cell (that is, the  $\vec{G}=0$  Fourier component) of the deforma-

tion potential,  $\langle \delta V^H \rangle$ , referring the Fermi energy and all the one-particle Hamiltonian eigenvalues to it.

Therefore, to compute with SIESTA the lineup term  $\Delta V_{SIESTA}$  that enters in the band-offset expression, we must apply the macroscopic average technique on the microscopic deformation potential  $\delta V^H$ , output of the self-consistent calculation for the supercell, comparing afterwards the plateau values at the two *bulklike* regions, as explained in the text. This method gives rise to a correct final band offset, although the decomposition into the band structure and the lineup term is not the standard one.

As this convention is unusual, in order to report values comparable to what could be computed with other codes, the results quoted in this paper are obtained following the *standard convention* ( $\langle V_{i+e}^H \rangle = 0$ ). Starting from the criterion of SIESTA ( $\langle \delta V^H \rangle = 0$ ), this can be done by (i) shifting rigidly the profile of the average of  $V_{i+e}^H$  [obtained by applying the macroscopic average technique to  $V_{i+e}^H(\vec{r})$  as it is dumped into a file by SIESTA] by subtracting the mean value

of the neutral-atom potential over the whole supercell and (ii) computing the lineup term  $\Delta V$ , comparing the plateaus from the previous profile. At a heterojunction  $A/B$ ,

$$\begin{aligned} \Delta V &= \langle V_{i+e}^H \rangle(B) - \langle V_{i+e}^H \rangle(A) \\ &= \langle V_{NA} \rangle(B) + \langle \delta V^H \rangle(B) - \langle V_{NA} \rangle(A) - \langle \delta V^H \rangle(A) \\ &= \langle V_{NA} \rangle(B) - \langle V_{NA} \rangle(A) + \Delta V_{SIESTA}, \end{aligned} \quad (A5)$$

where  $\langle V \rangle(B)$  stands for the value of the potential profile in the  $B$  region of the supercell. Because we now take into account the difference of the mean values of  $V_{NA}$  in the lineup term, we have to (iii) subtract them from the band structure term. Since the neutral-atom potential is short range and local, its average in the *bulklike* regions will not depend on the details of the interface. Consequently, it can be deduced from two independent calculations in the bulk of each material (it is a bulk quantity). The final result following this method is exactly the same as the one obtained from the procedure explained in the previous paragraph.

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