First-principles study of metal-induced gap states in metal/oxide interfaces and their relation with the complex band structure. Supplemental Material

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I. SCHEMATIC REPRESENTATION OF METAL-INDUCED GAP STATES (MIGS).

Suppl. FIG. 1. Schematic representation of metal-induced gap states in a metal/insulator interface. In (a), the wave function of an electronic state with an eigenvalue within the insulator band gap takes the form of a propagating wave function in the metallic side that decays exponentially on the insulating side. A schematic representation of the band alignment of the interface is shown in (b). MIGS below the Fermi level of the junction are populated and the resulting injection of charge is an important contribution to the interfacial dipole that determines the band alignment.

II. COMPUTATIONAL DETAILS.

Simulations on this work have been performed within the local density approximation (LDA) in the Ceperley-Alder parametrization as implemented in two different codes: SIESTA for the simulation of realistic capacitors, and the QUANTUM-ESPRESSO package for the complex band structure calculations. The use of two different codes is a delicate issue and thus keeping strict convergence criteria becomes critical in order to ensure the compatibility of all the simulations.

In order to simulate the effect of the mechanical boundary conditions due to the strain imposed by the substrate, in all the simulations the in-plane lattice constant was fixed to the theoretical equilibrium lattice constant of bulk SrTiO$_3$ ($a = 3.85$ Å for QUANTUM-ESPRESSO and $a = 3.874$ Å for SIESTA).

During the structural optimizations of both bulk PbTiO$_3$ and the capacitors, a Monkhorst-Pack mesh equivalent to $12 \times 12 \times 12$ in a perovskite unit cell was used for the sampling of the reciprocal space. Tolerances for the forces and stresses were 0.01 eV/Å and 0.0001 eV/Å$^3$, respectively. Other computational parameters, specific to each code, are summarized below.
A. QUANTUM-ESPRESSO

Complex band structure of bulk PbTiO$_3$ has been calculated using a density-functional plane-wave code with pseudopotentials. We have used the ultrasoft Vanderbilt pseudopotentials tabulated in the Vanderbilt Ultra-Soft Pseudopotential Site. The plane-wave cutoff was set to 40 Ry. For the generation of the 2D-histogram of Fig. 1(d) of the main body of the manuscript, a 48 × 48 mesh of $k$∥ points over the two-dimensional Brillouin zone (2DBZ) was sampled.

B. SIESTA

Computations on short-circuited Pt/PbTiO$_3$ and SrRuO$_3$/PbTiO$_3$ capacitors were performed using a numerical atomic orbital method, as implemented in the SIESTA code. Core electrons were replaced by fully-separable norm-conserving pseudopotentials, generated following the recipe given by Troullier and Martins. Further details on the pseudopotentials and basis sets can be found in Ref. 12.

A Fermi-Dirac distribution was chosen for the occupation of the one-particle Kohn-Sham electronic eigenstates, with a smearing temperature of 8 meV (100 K). The electronic density, Hartree, and exchange-correlation potentials, as well as the corresponding matrix elements between the basis orbitals, were computed on a uniform real space grid, with an equivalent plane-wave cutoff of 1200 Ry in the representation of the charge density.

The capacitors were simulated by using a supercell approximation with periodic boundary conditions. A (1 × 1) periodicity of the supercell perpendicular to the interface is assumed. This inhibits the appearance of ferroelectric domains and/or tiltings and rotations of the O octahedra. A reference ionic configuration was defined by piling up a number of unit cells of the perovskite oxide (8.5 for the SrRuO$_3$-based capacitor and 6.5 for the Pt-based capacitor), and 9.5 unit cells of the metal electrode. The PbTiO$_3$ films are always terminated in a TiO$_2$ atomic layer.

To simulate the capacitors in a non polar configuration, we imposed a mirror symmetry plane at the central TiO$_2$ layer, and relaxed the resulting tetragonal supercells within $P4/mmm$ symmetry. For the ferroelectric capacitors a second minimization was carried out, with the constraint of the mirror symmetry plane lifted. We have checked that the band-alignment in all systems reported here is non-pathological.

III. BULK BAND STRUCTURE OF PbTiO$_3$.

We compare complex band structure calculations on bulk PbTiO$_3$ with properties of MIGS in capacitors where the out-of-plane cell vectors were allowed to relax. As required by the strong sensitivity of complex bands on the real band structure, bulk calculations must be performed under the same symmetry constraints applied to the PbTiO$_3$ layer in the capacitor. It is important to note here that the bulk paraelectric phase discussed in this work is not the cubic phase, but a tetragonal centrosymmetric $P4/mmm$ phase. The in-plane lattice constant was fixed to the theoretical one of SrTiO$_3$ and the out-of-plane stress was relaxed while the atomic positions were kept in the centrosymmetric positions.

Given the sensitivity of complex bands to the size of the gap and the curvature of real bands they connect with, a good agreement between the band structures obtained with both codes is required to obtain comparable results. Suppl. Fig. 2 shows that the band structures calculated with the two different codes are virtually identical in shape, although the QUANTUM-ESPRESSO calculation displays a slightly larger gap. This must be taken into account since, in principle, a larger gap should translate into slightly larger values of the imaginary part of the complex wave vectors.

IV. DETAILS ON THE ANALYSIS OF MIGS IN FIRST-PRINCIPLES SIMULATIONS OF CAPACITORS.

The analysis of MIGS in full capacitor simulations requires to work with some sort of energy-resolved probability density. For this, a spatially resolved density of states is defined as

$$\rho(i, E) = \sum_n \int_{\text{BZ}} d\mathbf{k} |\langle \mathbf{i} | \psi_n \rangle|^2 \delta(E - E_n),$$

where $|i\rangle$ is a normalized function, localized in space around the region of interest.
When $|i\rangle = |r\rangle$ is an eigenstate of the position operator, the resulting $\rho(r, E)$ is commonly known as local density of states. However, strong oscillations of this function due to the underlying atomic structure difficult the analysis. Alternatively, the nanosmoothed version of this function might be used, but some interfacial properties, like precisely the decay length of the MIGS charge in the band gap, are sensitive to the specific convolution function used for the nanosmoothing procedure.\textsuperscript{16}

A reasonable choice is to work with the layer-by-layer ($z$-resolved) PDOS ($E$-resolved), defined as in Eq. (1) where $|i\rangle = |\varphi_{nlm}\rangle$ is an atomic orbital of specified quantum numbers ($n, l, m$). In this case the bias of the method lies in the choice of the basis of atomic orbitals. A sufficiently converged basis should minimize its effect since atoms of the same species at different sites are equally described, so the $z$ dependence might be considered as less biased than with previous methods. In Fig. 2 of the main body of the manuscript we plot the layer-by-layer PDOS corresponding to the PbTiO$_3$/SrRuO$_3$ capacitor.

The energy distribution of the charge density converges much slower with the $k$-point sampling than its spatial distribution. For this reason the PDOS was calculated performing an extra non-self consistent calculation with a finer $k$-point grid of $54 \times 54 \times 9$.

V. SYMMETRY FILTERING AT THE PbTiO$_3$/SrRuO$_3$ INTERFACE

Fig. 3(b) of the main body of the text of this work reveals some differences in the properties of MIGS of capacitors with SrRuO$_3$ or Pt electrodes. The dependence of the effective decay factor with the energy is essentially featureless in the case of Pt electrodes, while for SrRuO$_3$ this curve presents some structure. The most remarkable characteristic in the latter case is a sharp increase in the effective imaginary wave vector in the uppermost part of the PbTiO$_3$ gap, right above the Fermi level of the capacitor. This behavior is not due to intrinsic characteristics of the complex band structure of PbTiO$_3$ but to the interface.

The interface affects the energy dependence of the MIGS penetration mainly through the symmetry filtering: wave functions in the electrodes should match evanescent states in the insulator that are compatible by symmetry, filtering the complex bands that contribute to the effective value.

In Suppl. Fig. 3(a) we plot the complex band of minimum $q$ for paraelectric PbTiO$_3$ over the 2DBZ. We find that from the top of the valence band to the center of the gap, the bands with smaller $q$ are due to states in small circular (around $\bar{\Gamma}$) or square (around $\bar{X}$) regions centered at the high-symmetry points, while from energies between the middle of the gap and the bottom of the conduction band, the most penetrating bands come from $k_{\parallel}$ lying in a narrow rectangle centered along the $\bar{\Gamma}$ – $\bar{X}$ path. As can be seen in Fig. 1 of the main body of the manuscript, these deep-penetrating bands along the high symmetry $\bar{\Gamma}$ – $\bar{X}$ line are those that link to the bottom of the conduction band and have $\Delta_5$ symmetry at the $\bar{\Gamma}$ point.

The symmetry analysis of the band structure of bulk SrRuO$_3$, depicted in Suppl. Fig. 4(a), reveals that there is a band (highlighted in red) with the same symmetry as the evanescent states discussed above all along the $\bar{\Gamma}$ – $\bar{X}$ line, and that has its maximum around the Fermi level. For higher energies there are no bands with the appropriate symmetry to link the complex bands of minimal $q$ and form deep-penetrating MIGS. The matching has to be done with higher order complex bands with larger $q$. This explains the sharp increase of the effective imaginary part of the wave vector for energies above the Fermi level obtained in the PbTiO$_3$/SrRuO$_3$ capacitor.

For Pt there is a band with the appropriate $\Delta_5$ symmetry that crosses completely the band gap, as shown in Suppl.
Suppl. FIG. 3. (color online) (a) Minimum value of the imaginary part of the complex wave vector (maximum penetration) for bulk paraelectric PbTiO$_3$ over the 2DBZ. (b) DOS of SrRuO$_3$ over the 2DBZ. Both quantities are shown for eight different values of the energy, referred to the Fermi level of the PbTiO$_3$/SrRuO$_3$ capacitor. The center of each panel represents the Γ point, while the centers of each side symbolizes the X point.

Suppl. FIG. 4. (color online) Bulk real band structure of (a) bulk SrRuO$_3$ and (b) bulk Pt along the relevant directions in the 3-D Brillouin zone of the P$4/mmm$ tetragonal phase. The bands highlighted in red has symmetry $\Delta_5$ along the Γ-X line, and match complex bands in the PbTiO$_3$ with the same symmetry with $k_\parallel$ along the line Γ – X. The gray area indicates the band gap alignment of the PbTiO$_3$ layer for the corresponding capacitors.

Fig. 4(b). In other words, all the complex bands with minimum $q$ along the Γ – X path find a symmetry-compatible band in the Pt electrode to link with, explaining the featureless shape of $q_{\text{eff}}^{\text{MIGS}}$.

Other interface-intrinsic mechanism that could affect the energy dependence of the $q_{\text{eff}}^{\text{MIGS}}$ is the $k_\parallel$-dependence of the DOS of the metal. For instance, for a given energy, a DOS concentrated away from the high symmetry points Γ and X, or the high symmetry path Γ – X [where the most penetrating complex bands are found, see Suppl. Fig. 3(a)] would cause an increase of $q_{\text{eff}}^{\text{MIGS}}$ at that particular energy. This mechanism does not seem to contribute to the sudden increase of $q_{\text{eff}}^{\text{MIGS}}$ at the Fermi level in the SrRuO$_3$/PbTiO$_3$ capacitor: the DOS of SrRuO$_3$ varies smoothly with the energy and has a significant density around the high symmetry points and paths near the Fermi level [see Fig. 3(b)].

VI. DISCUSSION ABOUT THE EFFECT OF THE FERROELECTRIC POLARIZATION OF THE PbTiO$_3$ LAYER

Most of the discussions in the main text of the manuscript regard the paraelectric phase of the PbTiO$_3$/SrRuO$_3$ capacitor. However, PbTiO$_3$ is a ferroelectric perovskite with a large spontaneous polarization in bulk.$^{17}$ Indeed, the influence of the polarization in the spatial and energetic distribution of evanescent states in ferroelectric/metal interfaces has been proposed to contribute largely to the electro$^{18–20}$ and magnetoresistance$^{21–23}$ of ferroelectric
Suppl. FIG. 5. (color online) (a) Layer-by-layer PDOS of a polar \(\text{[SrRuO}_3]_9\)\textsubscript{5}/\(\text{[PbTiO}_3]_8\)\textsubscript{5} capacitor. The dashed line indicates the Fermi level. (b) Profile of the macroscopically-averaged electrostatic potential across the capacitor. (c) Effective imaginary wave vectors obtained from the fit of the decay of the PDOS of the PbTiO\(_3\) layer in the polar capacitor (black line), from the CBS of bulk PbTiO\(_3\) with the same ferroelectric distortion as in the center of the capacitor (blue line) and from the CBS of centrosymmetric PbTiO\(_3\) (red line). The two horizontal lines indicate the position of the Fermi level at the two interfaces (note that in the capacitor the Fermi level is the same across the whole structure, but to extract \(q_{\text{MIGS}}^{\text{Eff}}(E)\) the PDOS at each atomic layer is shifted following the electricstatic potential to align the band structures). (d) Complex band structure of centrosymmetric \(P4/mmm\) (red) and fully relaxed ferroelectric (blue) PbTiO\(_3\). The plot was obtained following the same recipe as for Fig. 1(d) of the main manuscript. Red and blue solid lines are the effective decays obtained from the CBS of centrosymmetric and polarized PbTiO\(_3\) respectively. Red and blue dashed lines correspond to the bottom of the conduction band in each case. The zero of energies in panels (c) and (d) is set to the top of the valence band.
tunnel junctions. A thorough analysis of such effect, using similar arguments as those developed in this paper, would be very useful in this regard. It should be noted, however, that the investigation of those aspects related with the realistic interfaces has the limitation imposed by the band alignment issues reported elsewhere\textsuperscript{14}, that restrict (i) the number of possible electrodes that can be tested within the usual approximations to the exchange-correlation functional (only for SrRuO\textsubscript{3}, a sizable polarization can be induced in the PbTiO\textsubscript{3} layer before causing the spurious electric breakdown of the capacitor) and (ii) the magnitude of the polarization (even for SrRuO\textsubscript{3} electrodes, the interface becomes pathological for polarizations of the PbTiO\textsubscript{3} layer larger than $\sim 40 \mu C/cm^2$).

For the capacitors discussed here, we find only the [SrRuO\textsubscript{3}]\textsubscript{9.5}/[PbTiO\textsubscript{3}]\textsubscript{8.5} capacitor to display a correct band alignment in the polar configuration, with a polarization of 24 $\mu C/cm^2$ after relaxing under short-circuit boundary conditions. Suppl. Fig. 5(a) displays the layer-by-layer PDOS in the PbTiO\textsubscript{3} film. The tilting of the bands due to the remnant depolarizing field is clearly appreciable. To extract the $q_{\text{MIGS}}^{\text{CBS}}$ from the PDOS using the same recipe developed in the main manuscript we have to take into account that here the band structure at different atomic layers is shifted as a result of the depolarizing field. To perform the fitting of the decay of the MIGS in the same fashion as in Fig. 3(a) of the main paper, we align the layer-by-layer PDOS using the macroscopic average of the electrostatic potential, shown in Suppl. Fig. 5(b). The resulting $q_{\text{MIGS}}^{\text{CBS}}(E)$ for the ferroelectric configuration of the SrRuO\textsubscript{3}/PbTiO\textsubscript{3} capacitor is shown as a black line in Suppl. Fig. 5(c). When compared with the $q_{\text{eff}}^{\text{CBS}}(E)$ obtained for bulk PbTiO\textsubscript{3} with the same ferroelectric distortion a good agreement is found, as in the paraelectric configuration. For such polarization (24 $\mu C/cm^2$) the change in the effective decay of MIGS induced by the ferroelectric distortion is not very large.

To appreciate better the effect of the ferroelectricity in the MIGS we compute the CBS for the fully relaxed bulk PbTiO\textsubscript{3} (which displays a polarization of 81 $\mu C/cm^2$ when the in-plane lattice constant is fixed to that of SrTiO\textsubscript{3}). The resulting $q_{\text{CBS}}^{\text{CBS}}$ is plotted in Suppl. Fig. 5(d).

The effect of the ferroelectric distortion on the band structure of PbTiO\textsubscript{3} is two-folded (see Suppl. Fig. 6). In first place it opens the gap, tending to increase the imaginary part of the complex bands wave vectors. In addition, it pushes up the flat band that constitutes the bottom of the conduction band along the $\Gamma$–X path in the paraelectric configuration. Suppl Fig. 5(d) shows that this increases greatly the imaginary part of those bands that link to the bottom of the conduction band with $k_\parallel$ along the $\Gamma$–X. Suppl. Fig. 5(d) also shows that, while complex bands at high symmetry paths of the 2DBZ are indeed strongly affected by the polarization of PbTiO\textsubscript{3}, the dense cluster of bands with $q \sim 0.2 (2\pi/c)$ display very little distortion in the polar state with respect to the non-polar one. The net result is a decrease of the penetration of MIGS, that is larger the closer the energy is to the conduction band, as evidenced by the estimated $q_{\text{CBS}}^{\text{CBS}}$ shown in Suppl Fig. 5(d).


9 See http://www.physics.rutgers.edu/ dhv/uspp/.