

# Supplementary Material: the Fundamental Asymmetry in Interfacial Electronic Reconstruction between Insulating Oxides

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(Dated: December 17, 2008)

**1. Computational details:** The calculation is performed using the code PWSCF[1]. The reference configurations of the ultrasoft pseudopotentials are: Sr  $4s^2 4p^6 5s^2$  ( $r_c^s = 2.0, r_c^p = 1.8$ ), Ti  $3s^2 3p^6 3d^1 4s^2$  ( $r_c^s = r_c^p = r_c^d = 1.8$ ), La  $5s^2 5p^6 5d^1 6s^{1.5} 6p^{0.5}$  ( $r_c^s = r_c^d = 2.2, r_c^p = 2.0$ ), Al  $3s^2 3p^1$  ( $r_c^s = 1.8, r_c^p = 1.82$ ) and O  $2s^2 2p^4$  ( $r_c^s = r_c^p = 1.3$ ) where the unit is the Bohr radius. The plane wave basis energy cutoff and charge cutoff are 30 Ry and 180 Ry, respectively. We use a Gaussian smearing width of 5 mRy when sampling the Brillouin zone. The  $k$ -grid sampling of the Brillouin zone is  $10 \times 10 \times 1$  where the  $z$ -axis is orthogonal to the interfaces. The convergence of the total energy and total charge density has been checked with  $k$ -grids of up to  $20 \times 20 \times 1$ .

**2. Simulation cells:** The periodic supercell used in our simulation is illustrated in Fig. 1. The interfaces are (001) in the horizontal  $z$  direction, and the unit cell is primitive ( $1 \times 1$ ) in the  $xy$  direction. Simulation cells are described by the nomenclature  $s_1 + l + s_2 + v$ .  $s_1$  and  $s_2$  are the numbers of STO unit cells;  $l$  is the number of LAO unit cells;  $v$  is the length of the vacuum region in units of the bulk STO lattice constant. The typical value of  $v$  in our calculation is 4 (i.e. about 15 Å). For the  $np$ -type interface, we choose  $s_1 = 5$  and  $s_2 = 5.5$  (the STO slab on the right is non-stoichiometric, terminated by an extra SrO layer — see section 3 for explanation). For the  $n$ -type interface,  $s_2$  is set to be zero and we choose  $s_1 = 11$ . For the  $p$ -type interface,  $s_2$  is set to be zero and we choose  $s_1 = 11.5$  (the STO slab on the left is terminated by an additional SrO layer). In all three cases,  $l$  is varied from 1 to 7. We relax all the atoms except for the two unit cells of STO adjacent to the STO-vacuum surface in order to simulate bulk-like substrates (see section 3 below). The inclusion of vacuum is necessary because without vacuum there would be an artificial electric field through STO due to the periodic boundary conditions. This field would unphysically polarize STO. From our calculations we also find that the polarized STO prevents the insulating-to-metallic transition from occurring. This is why the other studies have not shown the transition in similar calculations that do not include vacuum [2, 3].

**3. Surface effects:** The choice of STO slab termination facing the vacuum in our calculations is a technical but important detail: if not done with care, it could lead to misleading results. Specifically, using a  $\text{TiO}_2$  terminated STO surface creates a surface state that can contaminate the calculation. This phenomenon has also been observed by other researchers [4].

This issue is clearly illustrated by the comparison of two examples of  $p$ -type interface

calculations: (a) in Fig. 3 we show the oxygen projected density of states on the various atomic layers for the case  $5s+2l+5.5s+4v$ , where both STO surfaces are terminated by SrO layers, and (b) in Fig. 4 we show the same DOS but for  $5s+2l+6s+4v$ , where the rightmost surface is  $\text{TiO}_2$  terminated there. In the interior of both systems, the DOS look very similar and are bulk-like. However, the last (surface) layers differ significantly: the  $\text{TiO}_2$  terminated case (Fig. 4) has surface oxygen states with energies about 0.7 eV above the bulk valence band edge, and the position of the Fermi energy shows that holes are introduced into these surface cells. This behavior would in fact lead us to (incorrectly) conclude that  $l = 2$  is the critical thickness here.

This surface band is purely a surface phenomenon of STO and is not related to the presence of the LAO-STO interface. Fig. 5 shows the DOS for a symmetric slab of STO terminated by  $\text{TiO}_2$ , and we see the same behavior of the surface bands which are shifted 0.7 eV above the bulk valence band edge. SrO terminated STO slabs do not have such a shift. As we are aiming to simulate thick STO substrates in contact with the LAO-STO interfaces, these surface effects are not of interest, and serve only to mask the phenomenon we wish to examine. We minimize them by always using the SrO termination for our STO slabs.

Furthermore, we minimize any remaining surface effects by fixing the atomic geometry of the outermost two surface unit cells of STO to the bulk geometry (i.e. not relaxing those layers). This is the correct physical boundary condition: for a very thick STO substrate, as we move away from the interface and into the substrate the fields and perturbations due to the interface must die away leaving us with unpolarized and unperturbed STO bulk. The only remaining question is how thick the STO slab must be to approach the bulk behavior. We performed thorough convergence checks and find that 5 or more layers of STO are sufficient for convergence.

**3. Formation energy of oxygen vacancies:** We calculate the formation energy of oxygen vacancies in the bulk and at the  $p$ -type interface. The formation energy of oxygen vacancies is defined as the energy difference between a system with oxygen vacancies plus a corresponding number of isolated oxygen atoms and a defect-free system. Since it is argued in experiment that ideally 25% oxygen vacancies (mapped onto the plane of interface) lead to the insulating behavior at the  $p$ -type interface [5], our calculations employ a  $2 \times 2$  unit cell in the  $xy$ -plane. The density of oxygen vacancies is one oxygen vacancy out of  $2 \times 2 \times 5$  unit

cells of STO. As for the formation energy at the  $p$ -type interface, we include  $2 \times 2 \times 5$  unit cells of STO and  $2 \times 2 \times 1$  unit cells of LAO as well as  $\sim 16\text{\AA}$  thick vacuum. We consider three cases in which one oxygen vacancy is inserted in the first (closest to the interface), second and third SrO layers, respectively (see Fig. 2). The oxygen vacancies are in the SrO layers, as opposed to the  $\text{TiO}_2$  layers, in order to agree with the model proposed in [5]. The formation energy for this density of oxygen vacancies in the bulk is:

$$\Delta_{\text{STO-bulk}} = 10.356 \text{ eV} \quad (1)$$

The formation energy of an oxygen vacancy in the first, second and third SrO layer at the  $p$ -type interface are, respectively:

$$\Delta_{\text{IF-ov}}^1 = 11.092 \text{ eV} \quad (2)$$

$$\Delta_{\text{IF-ov}}^2 = 10.527 \text{ eV} \quad (3)$$

$$\Delta_{\text{IF-ov}}^3 = 10.481 \text{ eV} \quad (4)$$

From the formation energy, it is obvious that oxygen vacancies prefer to stay away from the  $p$ -type interface and diffuse into the bulk-like  $\text{SrTiO}_3$  substrate. This shows that a meaningful theoretical comparison is between pure  $n$ -type and  $p$ -type interfaces. It also supports our argument that the  $p$ -type interface is insulating because the delocalized holes in the  $\text{SrTiO}_3$  substrate are trapped by the oxygen vacancies since the bulk-like substrate is more energetically favorable for both of them than the  $p$ -type interface.

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- [1] PWSCF (Plane-Wave Self-Consistent Field) is a plane-wave pseudopotentials computer code for electronic structure calculations. <http://www.pwscf.org/>.
  - [2] S. Gemming and G. Seifert, *Acta Mater.* **54**, 4299 (2006)
  - [3] M. S. Park, S. H. Rhim and A. J. Freeman, *Phys. Rev. B* **74**, 205416 (2006)
  - [4] Jaekwang Lee and Alesander A. Demkov, *Mater. Res. Soc. Symp. Proc. Vol. 966@2007 Materials Research Society*, 0966-T07-33
  - [5] N. Nakagawa, H. Y. Hwang and D. A. Muller, *Nature Mater.* **5**, 204 (2006)

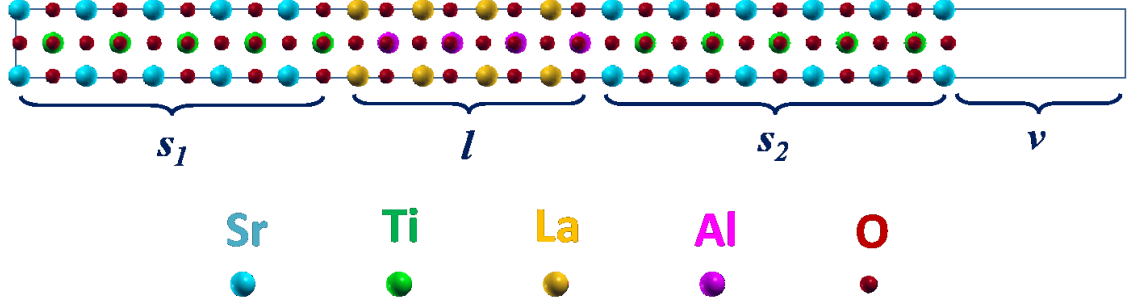


FIG. 1: Illustration of super cell in our simulation. The horizontal direction is the (001) direction and the cells are periodic in the  $xy$  plane.  $s_1$  and  $s_2$  denote the number of SrTiO<sub>3</sub> unit cell,  $l$  denotes the number of LaAlO<sub>3</sub> unit cell and  $v$  denotes the thickness of vacuum (in units of the bulk STO lattice constant).

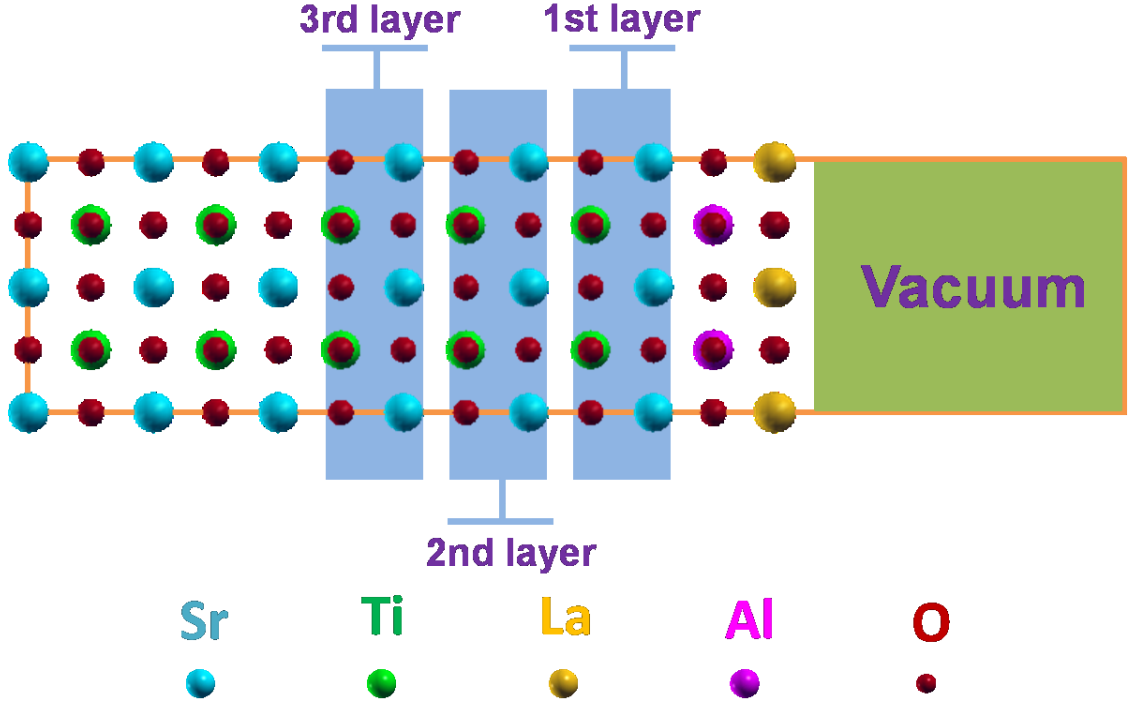


FIG. 2: Illustration of the super cell for the calculation of oxygen vacancy formation energies. The supercell is  $2 \times 2$  unit cell in the  $xy$  plane. Along the  $z$ -direction, there are 5 unit cells of STO plus 1 unit cell of LAO. The thickness of the vacuum is  $\sim 16\text{\AA}$ . The first layer of STO is defined as the one right at the  $p$ -type interface. The second and third layers are further away from the interface. The oxygen vacancy is inserted in the SrO of the first, second and third STO layers, respectively.

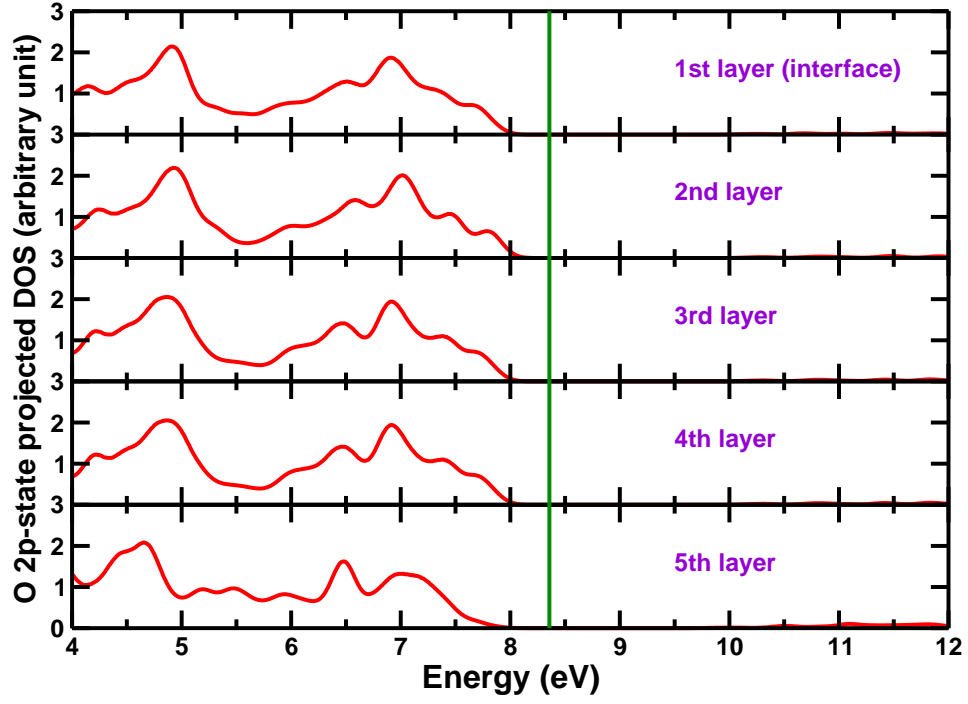


FIG. 3: Oxygen  $p$  projected density of states of the  $5s+2l+5.5s+4v$  system with SrO termination of both STO surfaces. The vertical green line is the Fermi energy. The O  $p$ -states in each  $\text{TiO}_2$  layer are approximately of the same energy and no surface state is observed.

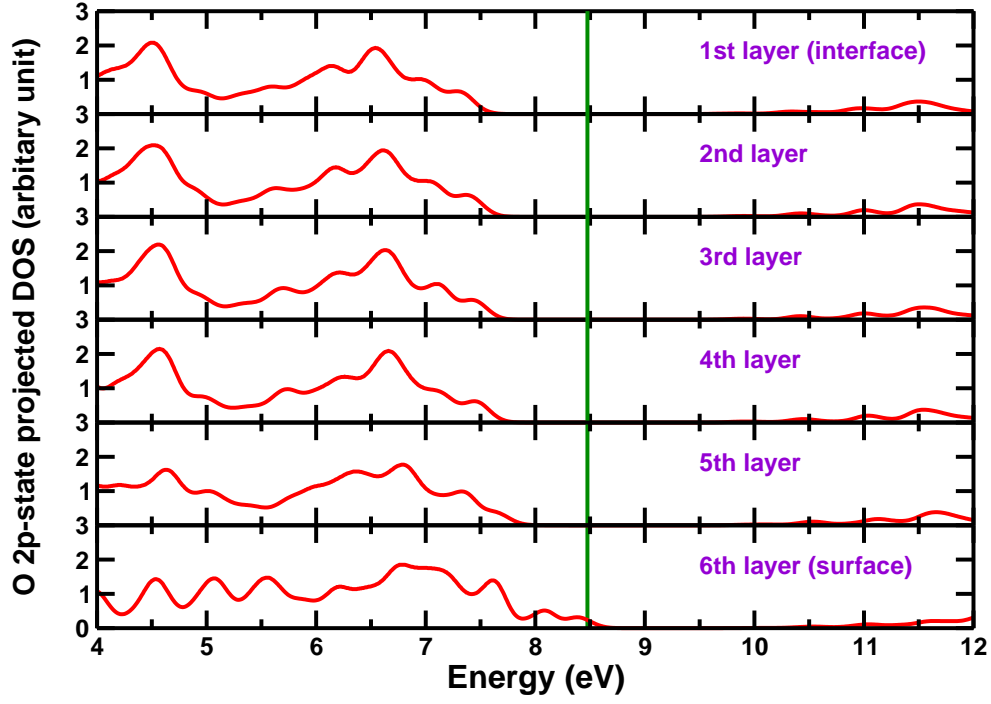


FIG. 4: Oxygen  $p$  projected density of states for the  $5s+2l+6s+4v$  system with  $\text{TiO}_2$  termination on the right surface. The vertical green line is the Fermi energy. The O  $p$ -state in the surface  $\text{TiO}_2$  layer is, compared to those in the STO slab, about 0.7 eV above the bulk valence band edge and is in fact partially filled with holes.

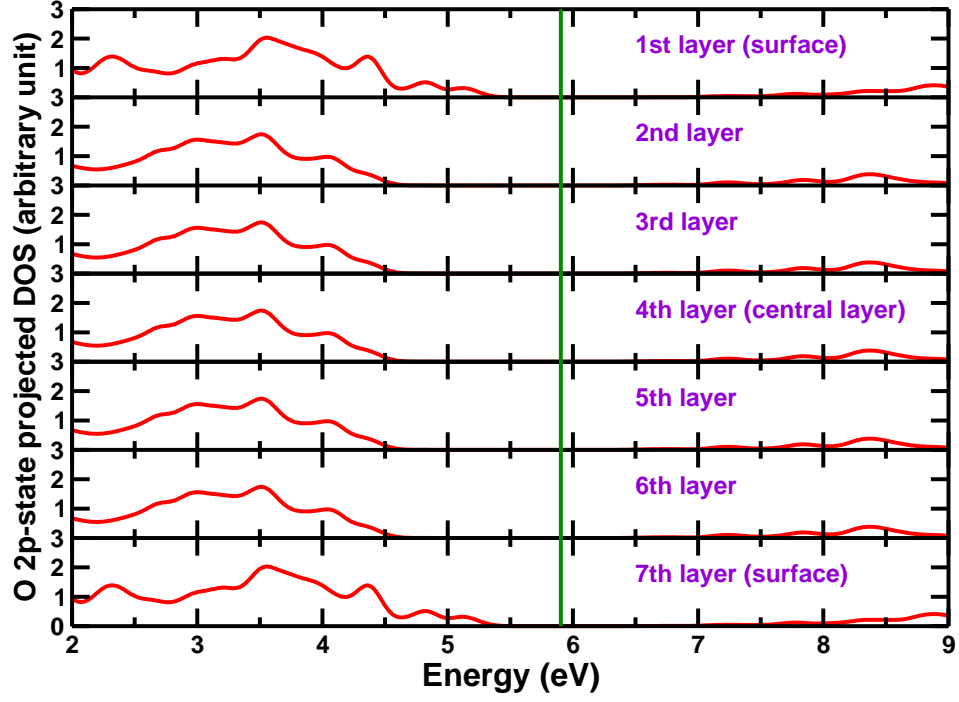


FIG. 5: Oxygen  $p$  projected density of states of an isolated symmetric STO slab with  $\text{TiO}_2$  termination. The vertical green line is the Fermi energy. The O  $p$ -states in the surface  $\text{TiO}_2$  layers are shifted compared to those in the central STO slab and lie about 0.7 eV above the bulk valence band, showing that this is a purely an STO surface effect, independent of LAO.