

Why some interfaces cannot be sharp

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A central goal of modern materials physics and nanoscience is the control of materials and their interfaces to atomic dimensions. For interfaces between polar and nonpolar layers, this goal is thwarted by a polar catastrophe that forces an interfacial reconstruction. In traditional semiconductors, this reconstruction is achieved by an atomic disordering and stoichiometry change at the interface, but a new option is available in multivalent oxides: if the electrons can move, the atoms do not have to. Using atomic-scale electron energy loss spectroscopy, we have examined the microscopic distribution of charge and ions across the (001) $\text{LaAlO}_3/\text{SrTiO}_3$ interface. We find that there is a fundamental asymmetry between the ionically compensated $\text{AlO}_2/\text{SrO}/\text{TiO}_2$ interface, and the electronically compensated $\text{AlO}_2/\text{LaO}/\text{TiO}_2$ interface, both in interfacial sharpness and charge density. This suggests a general strategy to design sharp interfaces, remove interfacial screening charges, control the band offset and, hence, markedly improve the performance of oxide devices.

Oxide thin films have already found a variety of industrial applications ranging from mainstream electronics to niche markets such as high-frequency filters. The wide variety of ground states available to the oxide family offers the potential for richer functionality than available with the present conventional semiconductors: from piezoelectric resonators to magneto-optical storage. In some cases, atomic-layer control of the growth is possible, presenting opportunities to couple different physical properties at the microscopic level. Several studies have demonstrated that, when interface effects dominate, the structure and stability at small lengthscales introduces a host of new considerations^{1–5}.

Electrostatic boundary conditions can be a dominant factor controlling the atomic and electronic structure at solid–solid interfaces. Even interfaces between formally neutral planes can have interface dipoles resulting from band offsets and bond polarizations^{6,7}. However, for materials with considerable ionic character, polar discontinuities introduce a larger energy cost for atomically abrupt heterointerfaces between planes of different polarity. This is the interface analogue of the divergent surface energy that would result from terminating a material along a polar plane with no surface reconstruction. The consequence for growing polar materials on nonpolar substrates (such as GaAs on Si or Ge) is a catastrophic roughening during growth, unless the composition is graded at the interface to ensure there is no net formal interface charge⁸. This grading results in a microscopically rough interface and, in many cases, also a measurable electrical band offset^{8,9}.

How the system responds to this energy cost will have consequences for both its electrical and physical properties, such as the creation of interface phases^{4,5,10} or differing interface roughness as a function of interface terminations. Much of this behaviour can be captured by a simple electrostatic model, which we discuss and test experimentally for (001) interfaces between SrTiO_3 , the workhorse oxide semiconductor, and LaAlO_3 , a closely lattice-matched insulator, useful as a gate dielectric for field-effect devices¹¹.

THEORY

The (001) planes in the ABO_3 perovskite structure can be divided into alternating layers of AO and BO_2 planes. Taking oxygen to

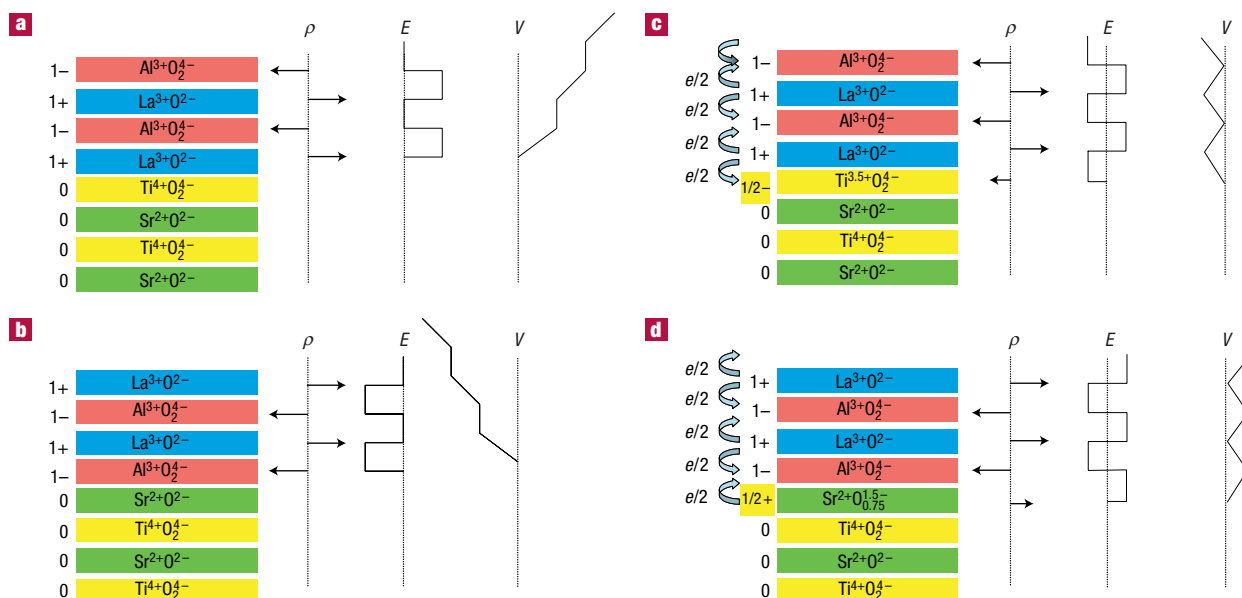


Figure 1 The polar catastrophe illustrated for atomically abrupt (001) interfaces between LaAlO_3 and SrTiO_3 . **a**, The unreconstructed interface has neutral (001) planes in SrTiO_3 , but the (001) planes in LaAlO_3 have alternating net charges (ρ). If the interface plane is $\text{AlO}_2/\text{LaO}/\text{TiO}_2$, this produces a non-negative electric field (E), leading in turn to an electric potential (V) that diverges with thickness. **b**, If the interface is instead placed at the $\text{AlO}_2/\text{SrO}/\text{TiO}_2$ plane, the potential diverges negatively. **c**, The divergence catastrophe at the $\text{AlO}_2/\text{LaO}/\text{TiO}_2$ interface can be avoided if half an electron is added to the last Ti layer. This produces an interface dipole that causes the electric field to oscillate about 0 and the potential remains finite. The upper free surface is not shown, but in this simple model the uppermost AlO_2 layer would be missing half an electron, which would bring the electric field and potential back to zero at the upper surface. The actual surface reconstruction is more complicated²¹. **d**, The divergence for the $\text{AlO}_2/\text{SrO}/\text{TiO}_2$ interface can also be avoided by removing half an electron from the SrO plane in the form of oxygen vacancies.

have a formal valence of O^{2-} , the A and B cations can take on values of $\text{A}^{4+}\text{B}^{2+}$, $\text{A}^{3+}\text{B}^{3+}$, $\text{A}^{2+}\text{B}^{4+}$ or $\text{A}^{1+}\text{B}^{5+}$, such that the ABO_3 bulk structure remains neutral. Fractional charge values also arise from solid solutions and/or mixed valence states. Just as compound semiconductors made from group IV elements such as Si or Ge have formally neutral (001) planes, the $\text{A}^{2+}\text{B}^{4+}\text{O}_3$ or ‘II–IV’ structure (such as SrTiO_3) also contains neutral AO and BO_2 (001) planes. An analogue of the III–V or II–VI semiconductors such as GaN or CdTe that have polar planes is the $\text{A}^{3+}\text{B}^{3+}\text{O}_3$ or ‘III–III’ structure (such as LaTiO_3 or LaAlO_3), which is composed of +1 AO and –1 BO_2 planes.

If we consider joining perovskites from two different charge families with atomic abruptness in an (001) orientation, a polar discontinuity results at the interface. Taking the example of joining LaAlO_3 with SrTiO_3 , two configurations arise, which can be defined by the composition of the layer between AlO_2 and TiO_2 at the interface: $\text{AlO}_2/\text{LaO}/\text{TiO}_2$ or $\text{AlO}_2/\text{SrO}/\text{TiO}_2$. Such a junction between polar and nonpolar planes is very common in oxide heterostructures, and the following discussion applies generally to many perovskite interfaces. Figure 1a,b shows how an atomically abrupt interface between polar and neutral layers leads to a polar catastrophe (where the electrostatic potential diverges with thickness) if there is no redistribution of charges at the interface.

Unlike conventional semiconductors where each ion has a fixed valence, in complex oxides compositional roughening is not the only option for charge rearrangement: mixed valence charge compensation can occur if electrons can be redistributed at lower energy cost than redistributing ions. Conceptually, one can first construct the interface from neutral atoms and then allow ionization, resulting in the net transfer of half an electron per two-dimensional unit cell ($e^-/\text{u.c.}$) from LaAlO_3 to SrTiO_3 across the interface (Fig. 1c). This process leaves the overall

structure neutral, with the Ti ion at the interface becoming $\text{Ti}^{3.5+}$, and the potential no longer diverges. The extra half an electron at the $\text{AlO}_2/\text{LaO}/\text{TiO}_2$ (‘n-type’) interface should be physically detectable by transport and direct spectroscopic measurements. Indeed, metallic conductivity and Hall measurements suggest free electrons at the n-type interface¹⁰. Figure 1d shows the analogous construction for the $\text{AlO}_2/\text{SrO}/\text{TiO}_2$ interface where the SrO layer must now acquire an extra half a hole per two-dimensional unit cell ($e^+/\text{u.c.}$) to maintain charge neutrality, that is, formally it should be ‘p-type’. Electrically, however, this interface is insulating¹⁰. As this positive charge is still electrostatically necessary to avoid the divergence, and there are no available mixed-valence states to compensate for the half a hole (such as $\text{Ti}^{4.5+}$, which is energetically inaccessible), an atomic reconstruction is required.

Here we show direct experimental evidence that the induced interface charges at the $\text{AlO}_2/\text{LaO}/\text{TiO}_2$ interfaces are compensated for by mixed-valence Ti states that place extra electrons in the SrTiO_3 conduction band. In contrast to this electronic interface reconstruction, the $\text{AlO}_2/\text{SrO}/\text{TiO}_2$ interface is compensated by the introduction of oxygen vacancies at the interface, an atomic interface reconstruction. For repeated growth of polar interfaces in $\text{LaAlO}_3/\text{SrTiO}_3$ superlattices, the cations intermix rapidly to reduce the interface dipole energy, representing a fundamental limit on the growth stability of multiple polar interfaces.

RESULTS

To understand the electrical asymmetry between the two interface terminations, we examined the interfaces with atomic-resolution electron energy loss spectroscopy (EELS) performed in a scanning transmission electron microscope (STEM) with single atom and vacancy sensitivity^{12,13}. Atomic-scale measurements of composition

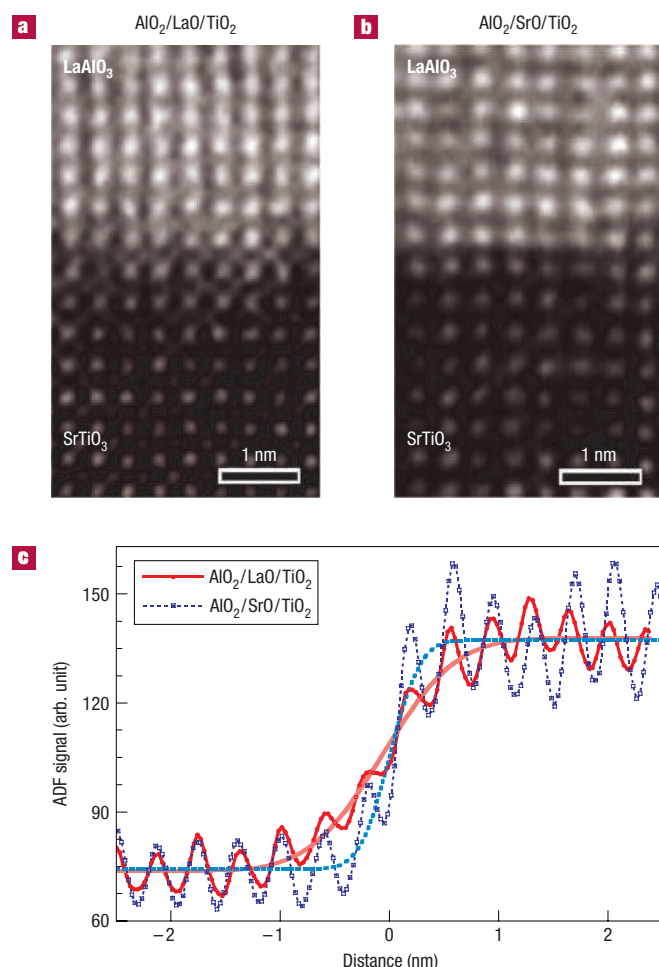


Figure 2 ADF-STEM images of the interface structures. La ions are brightest, followed by Sr, with the Ti occasionally faintly visible in between (the contrast is insufficient to resolve the Al or O ions). **a**, LaAlO₃ grown on TiO₂-terminated SrTiO₃ (forming the AlO₂/LaO/TiO₂ interface). **b**, LaAlO₃ grown on SrO-terminated SrTiO₃ (forming the AlO₂/SrO/TiO₂ interface). **c**, Averaged line profiles across the interfaces of **a**, **b**. An error-function curve is fit to both profiles to extract the average interface width. After accounting for a 0.2 nm probe size, the r.m.s. roughness for the AlO₂/LaO/TiO₂ interface of **a** is $\sigma = 1.90 \pm 0.11$ u.c., and for the AlO₂/SrO/TiO₂ interface of **b**, $\sigma = 0.77 \pm 0.13$ u.c.

and electronic structure at buried interfaces are possible^{13–15} using EELS from a high-energy (200 keV) electron beam focused down to a spot as small as 1–3 Å. By passing such a small electron beam through a thinned section, the excited states of atoms in their bulk environment can be probed. Electron-transparent cross-sectioned samples have been prepared by tripod polishing with water-free lubricants, followed by low-energy low-angle ion milling on a liquid-nitrogen-cooled stage. The wedge geometry allows us to examine the interface as a function of sample thickness, thereby separating out potential surface damage from the underlying bulk properties. We collect only small-angle inelastic scattering (<20 mrad), a regime in which the shape of the EELS signal becomes formally equivalent to that obtained from X-ray absorption spectroscopy¹⁶. The remaining high-angle (>50 mrad) scattering is predominantly elastic, and is used to form a simultaneously recorded annular dark field (ADF) image, with the heaviest atoms appearing the brightest¹⁷.

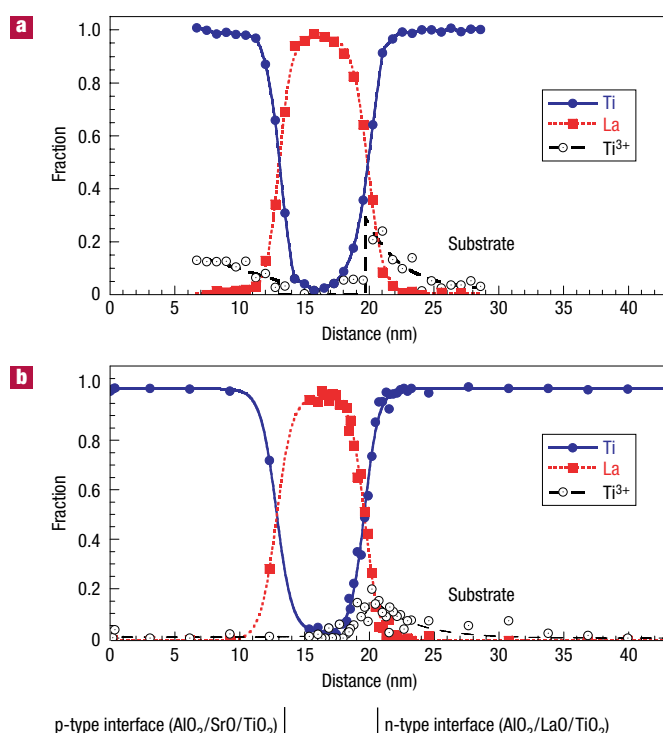


Figure 3 SrTiO₃/LaAlO₃/SrTiO₃ multilayer. **a**, Before and **b**, after annealing. The growth direction is right to left. The lower interface remains metallic and unchanged after annealing. The upper interface was insulating (no Ti³⁺) before annealing, even though the SrTiO₃ layer above it contained oxygen vacancies. After annealing, the vacancies have been filled. Also note from **a** that the upper interface (p-type) is less diffuse than the lower interface (n-type).

Figure 2 shows the interface structure of the LaAlO₃ films grown on SrTiO₃. The structures in this study were grown by pulsed laser deposition in an ultrahigh-vacuum chamber on atomically flat, TiO₂-terminated (001) SrTiO₃ single-crystal substrates. LaAlO₃, SrTiO₃, SrO single crystal targets and La₂Ti₂O₇ polycrystalline targets were used for two-dimensional layer-by-layer growth, as monitored by unit-cell reflection high-energy electron diffraction intensity oscillations throughout growth. The structures were grown at 750 °C under an oxygen partial pressure (P_{O_2}) of 1×10^{-5} torr, after pre-annealing the substrate at 960 °C in $P_{O_2} = 5 \times 10^{-6}$ torr for 30 min to removed surface contaminants. The laser spot was formed just off of the focusing condition with an average fluence of 3 J cm^{-2} , operating at a repetition rate of 5 Hz. We find that the AlO₂/LaO/TiO₂ interface is twice as rough as the AlO₂/SrO/TiO₂ interface (Fig. 2c). Even when the order of growth is switched and SrTiO₃ is grown atop LaAlO₃, the upper AlO₂/SrO/TiO₂ interface is still more abrupt than the lower AlO₂/LaO/TiO₂ interface (Fig. 3). Also shown in Fig. 3 is a comparison of as-grown interfaces with those annealed at 550 °C in O₂ for 4 h. In all cases, we found no change in the interface atomic or electronic structure with annealing. The effect of annealing was to fill residual oxygen vacancies in SrTiO₃ film layers, as well as improving the crystallinity of the film, therefore data from the annealed interfaces are presented here.

Figure 4a shows that as we continue to grow repeated LaAlO₃/SrTiO₃ multilayers, the interface roughness rapidly increases with each added multilayer. These structures were grown after monolayer deposition of SrO, followed by the repeated

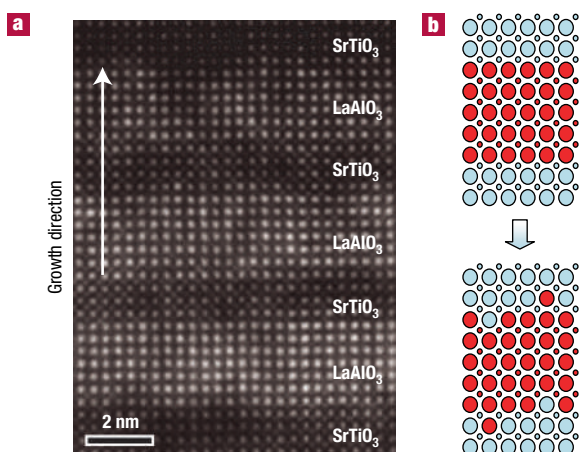


Figure 4 Repeated growth of $\text{LaAlO}_3/\text{SrTiO}_3$ multilayers. **a**, A $\text{LaAlO}_3/\text{SrTiO}_3$ multilayer structure composed of all n-type interfaces shows a progressive increase in interface roughness with growth. **b**, A schematic of the cation intermixing observed in **a**. The large blue circles are Sr, small blue for Ti, large red for La and small red for Al.

growth sequence (1 u.c. of LaTiO_3 , 4 u.c. of LaAlO_3 , 4 u.c. of SrTiO_3). In this manner, the superlattice is entirely composed of $\text{AlO}_2/\text{LaO}/\text{TiO}_2$ interfaces, hence the insertion of 1 u.c. of LaTiO_3 at the leading interface with LaAlO_3 . By this construction, simple La/Sr interdiffusion cannot remove the polar discontinuity, as illustrated schematically in Fig. 4b.

The microscopic distribution of formal valences is probed using EELS where the Ti-L, O-K and La-M edges are recorded simultaneously. The Ti-L edge provides a useful fingerprint of the Ti^{3+} and Ti^{4+} states from which a Ti d electron count and crystal-field symmetry can be extracted by least-squares fit to reference spectra^{4,13,18,19}. The O-K edge is also sensitive to the presence of oxygen vacancies and more extended features in the band structure^{13,20}. This richness makes it less amenable to an atomistic description. Instead, Fig. 5 shows that for the p-type interface the main features in the O-K edge spectra can be captured by a least-squares fit to reference spectra from bulk SrTiO_3 , bulk LaAlO_3 and oxygen-deficient $\text{SrTiO}_{3-\delta}$ with $\delta = 1/4$.

The lack of any statistically significant structure in the residual suggests that at our experimental sensitivity ($\sim 5\text{--}10\%$) and resolution (0.7 eV and 0.2 nm), the main changes in the local oxygen-bonding environment at the p-type interface are due to oxygen vacancies. Excluding the oxygen-deficient reference from the fit results in a significant residual, sharply peaked at the interface. EELS line profiles such as those of Fig. 5b were recorded for both interfaces. The integrated Ti, O and La counts give composition profiles, and least-squares fits to the Ti-L and O-K edge data resolve the variations in Ti valence and oxygen occupancy across the interface (see Figs 6 and 3). The quality of the fits can be evaluated from examining the lack of variation in the residuals.

The EELS-derived fractional compositions summarized in Fig. 6 resolve the puzzle over the electrical asymmetry between the n-type $\text{AlO}_2/\text{LaO}/\text{TiO}_2$ and p-type $\text{AlO}_2/\text{SrO}/\text{TiO}_2$ interfaces. We find that for the n-type interface (Fig. 6a), 0.7 ± 0.1 excess $e^-/\text{u.c.}$ are found on the Ti sites (non-zero Ti^{3+}) and very few oxygen vacancies ($0.1 \pm 0.04 \text{ V}_\text{O}/\text{u.c.}$). There are no excess electrons (0.1 ± 0.1) on the Ti sites for the p-type interface (Fig. 6c), where an extra half a hole would be expected theoretically. Instead, at the $\text{AlO}_2/\text{SrO}/\text{TiO}_2$ interface significant compensating oxygen

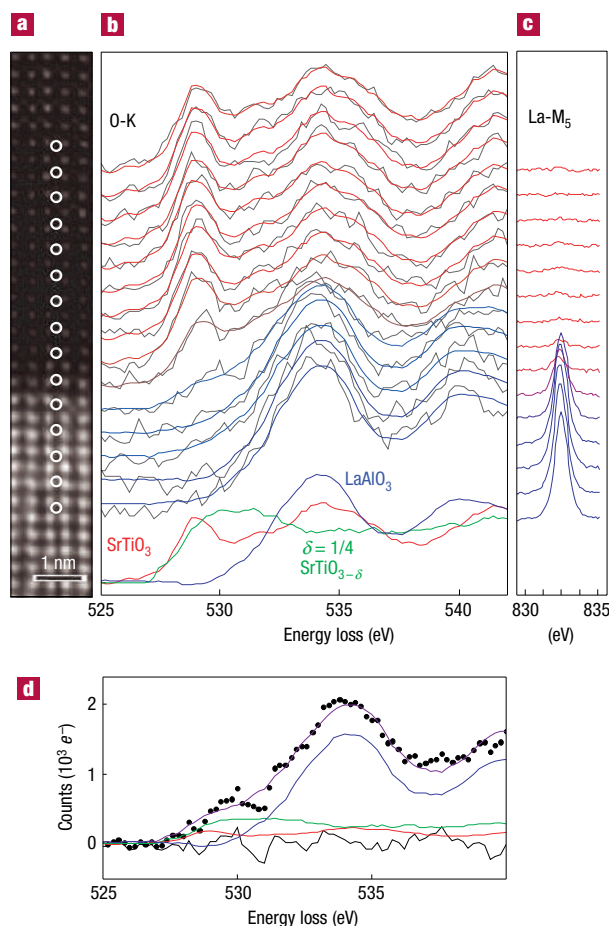


Figure 5 O-K edge EELS profile across a $\text{AlO}_2/\text{SrO}/\text{TiO}_2$ p-type interface. **a**, The ADF image of the interface: SrTiO_3 is the darker material in the upper half of the image and the LaAlO_3 film is in the lower half (scale bar 1 nm). **b**, O-K EELS spectra recorded from the circles in **a** (black curves). Bulk reference bulk spectra of O-K edges in SrTiO_3 (red curves), LaAlO_3 (blue curves) and $\delta = 1/4 \text{ SrTiO}_{3-\delta}$ (green curves) are shown at the bottom of the panel. The coloured lines show least-squares fits to the position-dependent spectra colour-coded by the fractional contribution of the red, green and blue reference spectra. **c**, The La-M edge (simultaneously recorded with the O-K data) showing the interface is graded over 2 u.c. **d**, The bottom panel shows the decomposition of the O-K edge at the interface in detail. Experimental data are shown as black data points, and the violet curve is the fit from the addition of the three reference spectra. The residual to the fit is given by the black curve at the bottom.

vacancies ($0.32 \pm 0.06 \text{ V}_\text{O}/\text{u.c.}$, which would imply 0.64 ± 0.12 fewer electrons at $2e^-$ per O) are present (Fig. 6d), but no free holes are found (which would give a pre-peak on the O-K edge). The EELS measurements suggesting free carriers at the n-type, but not the p-type interface are consistent with the electrical measurements, with the EELS deducing that the sheet carrier density at the n-type interface is close to $5 \times 10^{14} \text{ cm}^{-2}$ and confined to within a few nanometres of the interface.

DISCUSSION

The EELS results indicate that accommodation of the polar discontinuity is the driving force for the interface electronic and atomic reconstructions we have observed. Perhaps the most striking

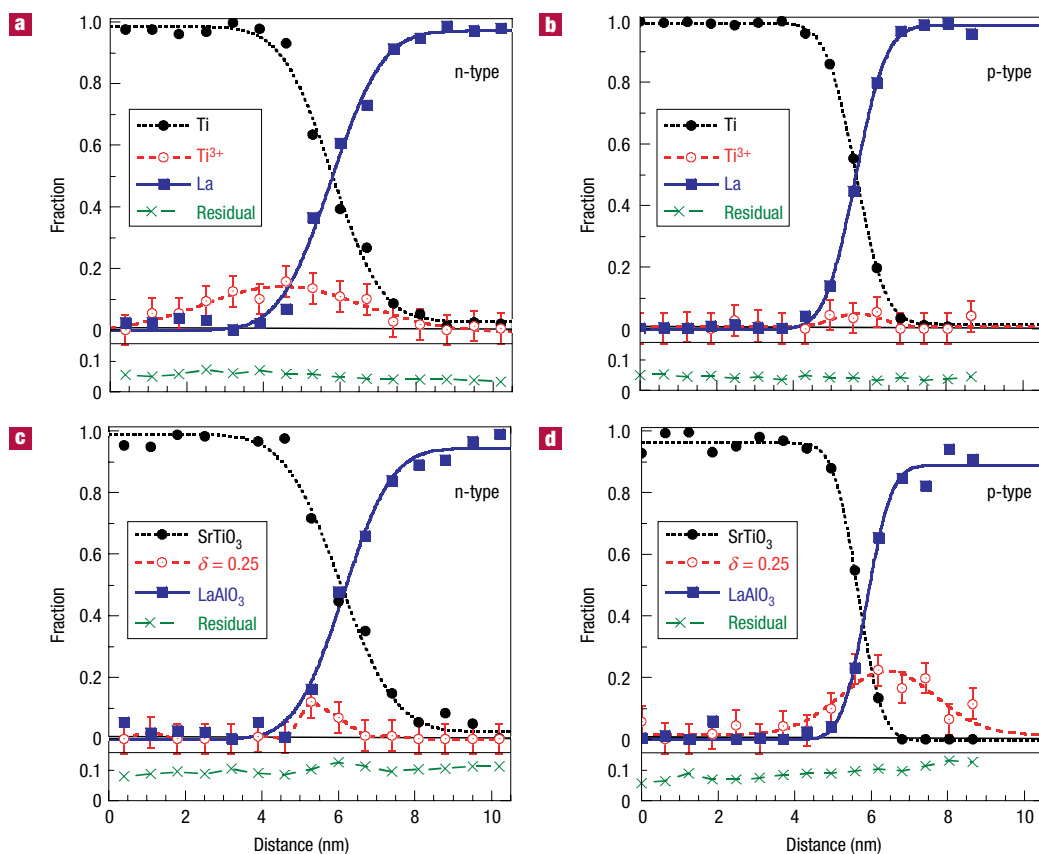


Figure 6 Chemical profiles of LaAlO_3 on (001) SrTiO_3 for both interface terminations. In each panel, the SrTiO_3 substrate is on the left and the LaAlO_3 on the right. **a**, $\text{AlO}_2/\text{LaO}/\text{TiO}_2$ interface showing the fractions of elemental Ti and La from the Ti-L and La-M edges, as well as the Ti^{3+} fraction determined from a least-squares fit to the Ti-L edge from Ti^{3+} and Ti^{4+} reference spectra. There is excess Ti^{3+} on the substrate side of the interface. **b**, Corresponding Ti and La EELS profiles for the $\text{AlO}_2/\text{SrO}/\text{TiO}_2$ interface, showing almost no excess Ti^{3+} . **c**, Fractional compositions from the least-squares fit to the O-K edge profile for the $\text{AlO}_2/\text{LaO}/\text{TiO}_2$ terminated interface, showing a net vacancy excess of $\delta = 0.1 \pm 0.04$. The labels are for the fits to the reference spectra as shown at the bottom of Fig. 5b. **d**, The O-K edge fractional composition (from Fig. 5b) for the $\text{AlO}_2/\text{SrO}/\text{TiO}_2$ interface showing a significant accumulation of excess vacancies ($\delta = 0.32 \pm 0.06$). The r.m.s. residual to the fits is shown below each plot.

point is that the interface with many oxygen vacancies has no excess electrons, whereas the interface with few oxygen vacancies has significant excess electrons. This is counter to the well-known role of oxygen vacancies in bulk oxides as electron donors, indicating that the origin and the function of the interface vacancies are completely different at the interface. This is bolstered by the fact that vacancies persist despite annealing in conditions far above those necessary to fill vacancies in thick $\text{SrTiO}_{3-\delta}$ films.

In comparing the valence profiles obtained from EELS with the simple model of half an electron per hole at the interface discussed in Fig. 1, the experimental data deviates from the model in two key respects. First, the electron are not fixed point charges, but delocalized in a screening cloud. This alters the size of the interface dipole but does not cause a divergence. Second, even though the net charge at the n-type interface is ~ 0.5 ($0.7 \pm 0.1 e^-$, $0.2 \pm 0.08 e^+$) there are more electrons than expected, which in turn are compensated for by slight oxygen vacancies, again altering the interface dipole.

In addition to the electrical asymmetry, why is there also an asymmetry in roughness? What we have ignored in this analysis so far is the delocalized electron cloud on the Ti sites at the $\text{AlO}_2/\text{LaO}/\text{TiO}_2$ interface. Spreading the electrons from a single plane to a few unit cells increases the interface dipole energy. This dipole can be reduced by exchanging Sr for La cations across

the interface to produce a compensating dipole, that is, physically roughening the interface. (In general, an exchange of ions can only produce a dipole, but not add or remove a diverging potential.) Without a delocalized screening electron or hole charge at the $\text{AlO}_2/\text{SrO}/\text{TiO}_2$ interface, there is less need to compensate for cation-mixing across the interface. Furthermore, distribution of the oxygen vacancies can provide any necessary compensating dipole. Both the EELS profiles of Fig. 6 and the images of Fig. 2 show that the n-type $\text{AlO}_2/\text{LaO}/\text{TiO}_2$ interface is indeed rougher than the $\text{AlO}_2/\text{SrO}/\text{TiO}_2$ interface.

The presence of a small number of oxygen vacancies ($\delta = 0.1 \pm 0.04$) at the n-type interface (which should ideally have $\delta = 0$) suggests a mechanism to reduce the band offset while still avoiding a divergence. Adding extra vacancies and compensating electrons to keep the same net charge introduces an interface dipole that will shift the band offset. Consider the case where $\delta = 0.125$ and we place the missing one-in-eight O atoms in the SrO plane, that is, the interface structure is $\text{SrO}_{0.875}/\text{Ti}^{3.25+}\text{O}_2/\text{LaO}/\text{AlO}_2$. This gives 0.75 excess $e^-/\text{u.c.}$ at the interface, but introduces no band offset (Fig. 7). In other words, the band offset can be tuned as a function of oxygen vacancy concentration, but with a price of adding electrons to the Ti conduction band at the interface.

A similar argument can be made for the p-type interface. The simplest interface of Fig. 1d would ideally have $\delta = 0.25$ and

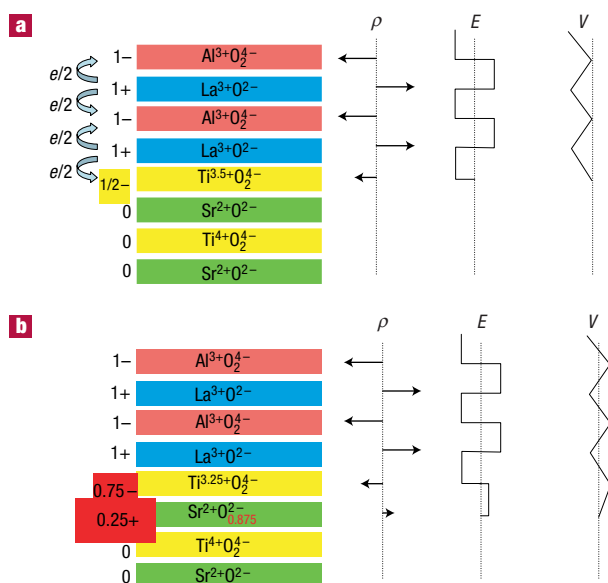


Figure 7 Tuning the band offset. **a**, The n-type interface of Fig. 1c where the average potential on the LaAlO_3 side is shifted by 0.46 V (the dipole shift assuming typical perovskite distances and performing the integral shown graphically). **b**, The band offset between SrTiO_3 and LaAlO_3 can be removed by adding an interface dipole composed of an extra 0.25 e^- on the interfacial TiO_2 layer, and an extra 0.125 oxygen vacancies on the next SrO layer. Overall, the net interface charge must remain at 0.5 to avoid a potential divergence.

one in four O atoms missing from the SrO plane, with no free electrons ($\text{Ti}^{4+}\text{O}_2/\text{SrO}_{0.75}/\text{AlO}_2/\text{LaO}$). The band offset can also be tuned for the p-type interface by removing O atoms and should have the same magnitude and opposite sign to the n-type case. The p-type interface with no band offset requires $\delta = 0.375$ and $\text{Ti}^{3.75+}\text{O}_2/\text{SrO}_{0.625}/\text{AlO}_2/\text{LaO}$, which gives 0.25 free electrons and three-in-eight missing O atoms in the SrO plane. The general case interpolates between $\delta = 0.25$ and 0.375. Experimentally, we find $\delta = 0.32 \pm 0.06$. The absence of a Ti^{3+} signal suggests the interface is closer to the ideal $\delta = 0.25$ (the lower end of the oxygen error range).

Controlling the interface termination layer lets us tune between insulator and conductor, trading chemical for electrical roughness. The band offset can be further adjusted by the oxygen-vacancy concentration, as discussed above, or by varying the cation ratio at the interface. Many oxide devices involve polar discontinuities at critical heterointerfaces such as in field-effect devices, tunnel junctions or ferroelectric/paraelectric interfaces. Our analysis

suggests that the interface screening charges that result from the inevitable polar discontinuities are, at present, comparable to or larger than the largest polarizations achievable in field-effect devices, and comparable to the best ferroelectric polarizations. By changing the substrate termination layer, the screening charge could be substantially reduced, which in turn should markedly enhance the performance of these devices, possibly by orders of magnitude.

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Competing financial interests

The authors declare that they have no competing financial interests.

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