

Nanoscale control of an interfacial metal-insulator transition at room temperature

C. Cen, Stefan Thiel, German Hammerl, Christof W. Schneider, K. E. Andersen, C. Stephen Hellberg, Jochen Mannhart, J. Levy

Angaben zur Veröffentlichung / Publication details:

Cen, C., Stefan Thiel, German Hammerl, Christof W. Schneider, K. E. Andersen, C. Stephen Hellberg, Jochen Mannhart, and J. Levy. 2008. "Nanoscale control of an interfacial metal-insulator transition at room temperature." *Nature Materials* 7 (4): 298–302. <https://doi.org/10.1038/nmat2136>.

Nutzungsbedingungen / Terms of use:

licgercopyright

Dieses Dokument wird unter folgenden Bedingungen zur Verfügung gestellt: / This document is made available under the following conditions:

Deutsches Urheberrecht

Weitere Informationen finden Sie unter: / For more information see:

<https://www.uni-augsburg.de/de/organisation/bibliothek/publizieren-zitieren-archivieren/publizieren>



Nanoscale control of an interfacial metal–insulator transition at room temperature

C. CEN¹, S. THIEL², G. HAMMERL², C. W. SCHNEIDER², K. E. ANDERSEN³, C. S. HELLBERG³, J. MANNHART² AND J. LEVY^{1*}

¹Department of Physics and Astronomy, University of Pittsburgh, 3941 O'Hara St., Pittsburgh, Pennsylvania 15260, USA

²Experimental Physics VI, Center for Electronic Correlations and Magnetism, Institute of Physics, University of Augsburg, D-86135, Augsburg, Germany

³Center for Computational Materials Science, Naval Research Laboratory, Washington, DC 20375, USA

*e-mail: jlevy@pitt.edu

Experimental^{1–7} and theoretical^{8,9} investigations have demonstrated that a quasi-two-dimensional electron gas (q-2DEG) can form at the interface between two insulators: non-polar SrTiO₃ and polar LaTiO₃ (ref. 2), LaAlO₃ (refs 3–5), KTaO₃ (ref. 7) or LaVO₃ (ref. 6). Electronically, the situation is analogous to the q-2DEGs formed in semiconductor heterostructures by modulation doping. LaAlO₃/SrTiO₃ heterostructures have recently been shown¹⁰ to exhibit a hysteretic electric-field-induced metal–insulator quantum phase transition for LaAlO₃ thicknesses of 3 unit cells. Here, we report the creation and erasure of nanoscale conducting regions at the interface between two insulating oxides, LaAlO₃ and SrTiO₃. Using voltages applied by a conducting atomic force microscope (AFM) probe, the buried LaAlO₃/SrTiO₃ interface is locally and reversibly switched between insulating and conducting states. Persistent field effects are observed using the AFM probe as a gate. Patterning of conducting lines with widths of ~ 3 nm, as well as arrays of conducting islands with densities $> 10^{14}$ inch⁻², is demonstrated. The patterned structures are stable for > 24 h at room temperature.

The success of semiconductors as technological materials is based on three important features: (1) their electrical conductivity can be tuned over a wide range, either by doping or through electric-field effects; (2) insulating layers (SiO₂) can be formed readily, enabling field-effect devices to be fabricated; (3) devices can be scaled to nanoscale dimensions. Oxide materials combine many of the important electronic properties of semiconductors^{10,11} with extra emergent phenomena, such as interfacial superconductivity¹², strain-driven ferroelectricity¹³, interfacial ferromagnetism¹⁴ and colossal magnetoresistance¹⁵.

The discovery of metallic and superconducting interfaces between insulating oxides has led to many subsequent investigations about the origin of this effect, and in particular the role played by oxygen vacancies^{16,17}. In samples that are heated to ~ 800 °C in high vacuum (order of 10^{-6} mbar), oxygen defects are created in the SrTiO₃ substrates which n-dope the material, regardless of the presence of a LaAlO₃ layer^{18–21}. For samples grown under oxygen pressures $\geq 10^{-5}$ mbar, as in the experiments described here, the interfacial conductance is dominated by the

potential profile generated between the SrTiO₃/LaAlO₃ interface and the top LaAlO₃ surface. Thiel *et al.* recently found that for samples with 3 unit cells of LaAlO₃, a bistable metal–insulator transition can be tuned with a voltage applied between the LaAlO₃/SrTiO₃ interface and the bottom SrTiO₃ substrate¹⁰, suggesting a role played by both the polar discontinuity and residual oxygen vacancies in the SrTiO₃.

Although oxides provide a wealth of opportunities for probing the rich physics of correlated electronic systems, for technological applications it is essential to scale device concepts to nanoscale dimensions. Ferroelectric field effects at ~ 350 nm scales have been reported for oxide heterostructures²². Here, we present a technique that can dynamically define at room temperature nanoscale conducting structures at the interface of two insulating oxides, LaAlO₃ and SrTiO₃, through reversible control of a localized metal–insulator transition. Both isolated and continuous conducting features with length scales well below 5 nm are demonstrated. Strong nonlinear electric-field effects are also observed. We suggest one possible theoretical explanation for this behaviour in terms of the creation of oxygen vacancies in the topmost LaAlO₃ surface.

The material system investigated here consists of 3 unit cells of LaAlO₃, grown at 770 °C in an O₂ pressure of 6×10^{-5} mbar by pulsed laser deposition on a TiO₂-terminated insulating SrTiO₃ substrate¹⁰. The samples were cooled in 400 mbar of O₂ with a 1 h oxidation step at 600 °C. Several samples were prepared under identical conditions and characterized. One of these samples was used for the studies described here. All measurements are carried out in air at 295 K. The sample is maintained in a dark environment to suppress carrier photoexcitation in SrTiO₃ (bandgap ~ 3.2 eV). A set of electrodes, in contact with the interface and spaced $D_0 = 150$ μ m apart, is fabricated using the techniques described in ref. 10.

A conducting atomic force microscope (AFM) tip, in contact with the top LaAlO₃ surface and biased at V_{tip} with respect to the interface, produces an interfacial metallic ($V_{\text{tip}} > 0$) or insulating ($V_{\text{tip}} < 0$) state directly below the area of contact. Note that V_{tip} is applied between the top LaAlO₃ surface and the LaAlO₃/SrTiO₃ interface; in the experiments of Thiel *et al.*¹⁰, the voltage was

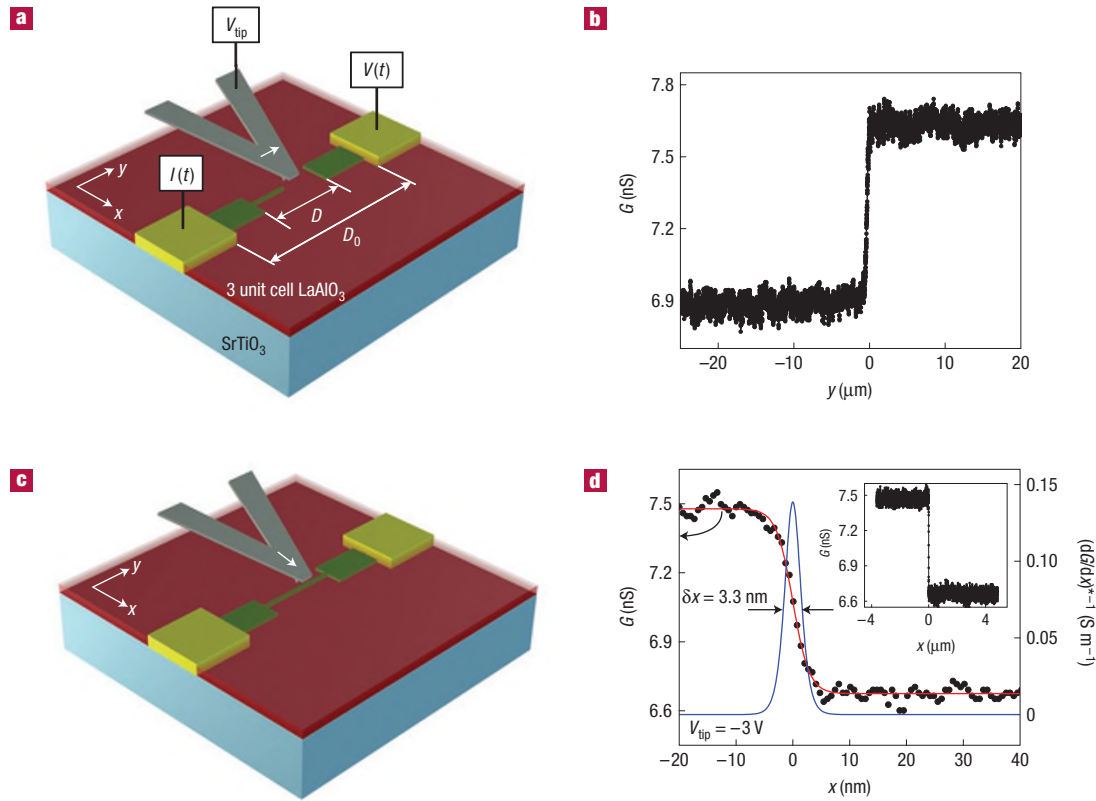


Figure 1 Writing and erasing nanowires at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface. **a**, Schematic diagram of the experimental set-up for writing a conducting wire. A voltage-biased AFM tip is scanned from one electrode towards a second one in contact mode. The tip generates an electric field that causes a metallic q-2DEG to form locally at the interface under the route of the tip. **b**, Conductance between the two electrodes measured with a lock-in amplifier as a function of the tip position while writing a conducting wire with 3 V bias applied to the tip. A steep increase in conductance occurs when the tip reaches the second electrode. **c**, Schematic diagram of the experimental set-up for cutting a conducting wire. The negatively biased AFM tip moves in contact mode across the conducting wire. The tip erases the metallic q-2DEG locally when it crosses the conducting wire. The conductance between two electrodes is monitored as the tip scans over the wire. **d**, Conductance between the two electrodes measured as a function of the tip position across the wire, while cutting the wire with the tip biased at -3 V . A sharp drop in conductance occurs when the tip passes the wire. The inset shows the conductance measured over the entire $8\ \mu\text{m}$ scan length. The decrease in conductance can be fitted to a profile $G(x) = G_0 - G_1 \tanh(x/h)$ with best-fit parameters given by $G_0 = 7.1\ \text{nS}$, $G_1 = 0.40\ \text{nS}$ and $h = 2.9\ \text{nm}$. The deconvolved differential conductance $(dG/dx)^{-1}$ showing a full-width at half-maximum $\delta x = 3.3\ \text{nm}$ is also plotted.

applied between the interface and the bottom SrTiO_3 substrate surface. For the experiment described below, the gap between the conducting electrodes is first reduced to $D = 40\ \mu\text{m}$ by ‘writing’ (that is, raster-scanning at $V_{\text{tip}} = +10\ \text{V}$) two rectangular pads (Fig. 1a). The electric conductance between the two electrodes is monitored using a lock-in amplifier. The AFM tip, now biased at $V_{\text{tip}} = +3\ \text{V}$, writes a line by scanning from one electrode to the other. As the tip reaches the second electrode, a pronounced and abrupt conductance increase $\Delta G \approx 0.8\ \text{nS}$ is observed (Fig. 1b). This increase is not associated with any observed topographic changes of the structure, nor is it affected by subsequent imaging by an electrically isolated or grounded probe.

To provide a measure of the transverse dimension of the conducting wire, and to demonstrate that the writing process is reversible, the wire is subsequently ‘cut’ with a reverse voltage $V_{\text{tip}} = -3\ \text{V}$ (Fig. 1c). As the AFM tip crosses the wire, the conductance decreases abruptly by $\Delta G \approx -0.8\ \text{nS}$ (Fig. 1d). Assuming the erasure process to have a resolution comparable to the writing process, the deconvolved differential profile $(dG/dx)^{-1}$ thus exhibits a full-width at half-maximum of $\delta x = 3.3\ \text{nm}$. Subsequent writing with positive voltages over the affected area (for example, $V_{\text{tip}} = +3\ \text{V}$) restores the conductance

of the wire. The wire width depends sensitively on V_{tip} , increasing by three orders of magnitude as V_{tip} is raised from $3\ \text{V}$ to $10\ \text{V}$. Test measurements were carried out over a 24 h interval and showed that the wires remain stable over that time frame.

The written wires are highly sensitive to externally applied electric fields. Figure 2a shows the current-voltage (I - V) characteristics of a $20\text{-}\mu\text{m}$ -long wire, created with $V_{\text{tip}} = 10\ \text{V}$, that has been perturbed by the AFM probe with varying voltages. The AFM probe functions much like the gate of a ferroelectric field-effect transistor, except that the probe can be scanned. For each curve, the AFM probe is set to a voltage V_{gate} and scanned once across the wire. Afterwards, the in-plane current I_{\parallel} is measured (using a picoammeter referenced to virtual ground) as a function of the voltage V_{sd} applied to one electrode. For low $|V_{\text{gate}}|$, the wire conductance is unaffected. However, as the tip bias becomes more negative, the wire becomes insulating and conducts only above a finite bias. This turn-on bias increases monotonically with $|V_{\text{gate}}|$. Eventually the I - V curve becomes asymmetric, the probable origin of which is an asymmetry in the insulating barrier profile, produced by unequal electric fields on both sides of the AFM tip.

It is also possible to write isolated conducting islands or ‘dots’ by applying voltage pulses $V_{\text{tip}}(t)$ with amplitude V_{pulse} and duration

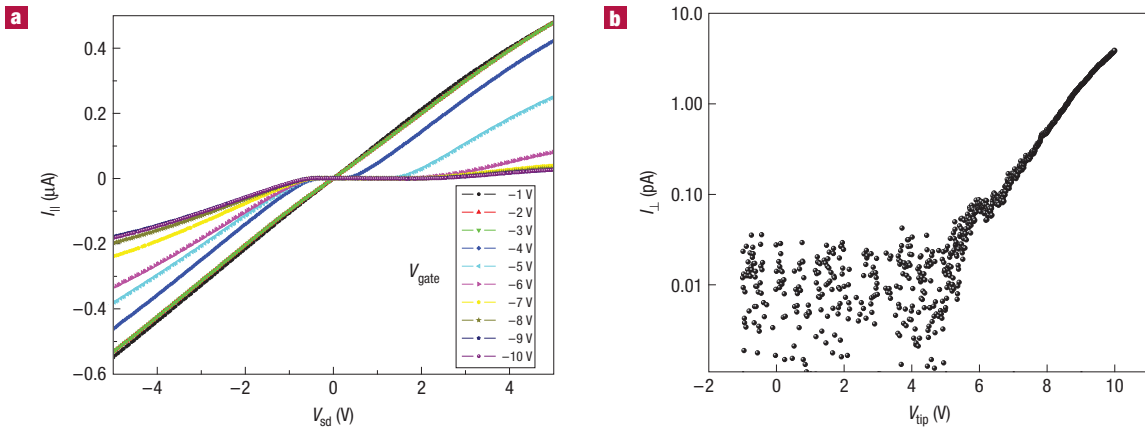


Figure 2 Current–voltage characteristics of $\text{LaAlO}_3/\text{SrTiO}_3$ interface. **a**, Current I_{\parallel} versus ‘source–drain’ voltage V_{sd} of a 20- μm -long q-2DEG wire with a potential barrier near the centre, created with a negative ‘gate’ bias V_{gate} . The barrier is created using the method shown in Fig. 1c. Different colours represent different tip biases. When the line is interrupted with a sufficiently large tip bias, the I – V characteristic becomes strongly nonlinear. Conducting behaviour is observed at large d.c. source voltages. **b**, AFM tip current I_{\perp} versus tip voltage V_{tip} with respect to grounded interface.

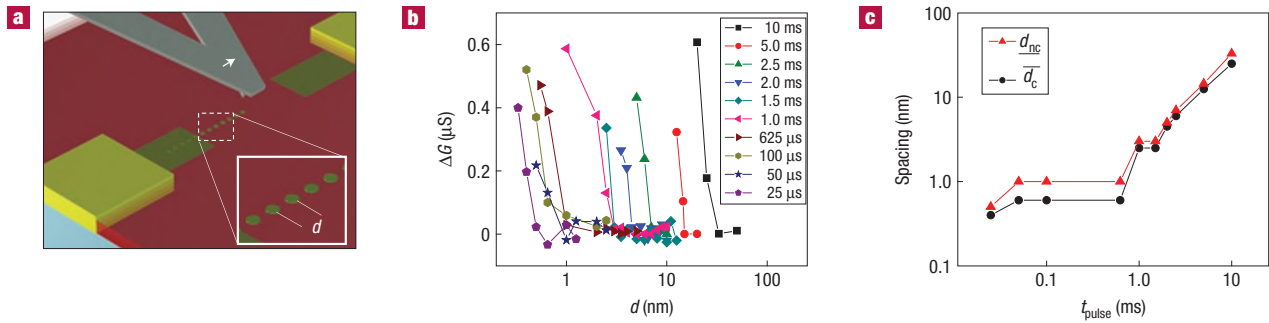


Figure 3 Measuring the limits of conducting island density. **a**, Schematic diagram showing a linear array of dots written with voltage pulses. **b**, Conductance change as the array is connected to electrodes, for various spacings between dots and different pulse durations. **c**, Plot of minimum dot spacing for which the array is non-conducting $\underline{d}_{\text{nc}}$ and the maximum dot spacing for which the array is conducting \overline{d}_c , presented as a function of pulse duration t_{pulse} .

t_{pulse} to the tip while keeping the tip at a fixed position. During pulsed writing the two electrodes are grounded. The size of the dots depends on both V_{pulse} and t_{pulse} . For simplicity, we keep $V_{\text{pulse}} = 10\text{ V}$ fixed and vary t_{pulse} to change the size of the dots. To determine the effective size of the dots, linear arrays of dots are created with various separations d (Fig. 3a). After writing the arrays, the ends of the arrays are contacted by writing conducting electrodes, which are separated by $D = 1\mu\text{m}$. As the contacts are being written, the conductance between the two electrodes is monitored using a lock-in amplifier. If the spacing between the dots is greater than the dot diameter, the dots will not overlap and no increase in conductance will be observed. Once the spacing becomes equal to or smaller than the dot diameter, the linear array will form a conducting wire, manifested as an abrupt increase in conductance between the two electrodes (ΔG), once the wire is attached. For each pulse duration, a sharp metal–insulator transition is observed as the dot spacing is reduced (Fig. 3b). The smallest non-conducting spacing $\underline{d}_{\text{nc}}$ and the largest conducting spacing \overline{d}_c are plotted as a function of t_{pulse} (Fig. 3c). The critical spacing for conduction \overline{d}_c is bound by these two measured quantities ($\underline{d}_{\text{nc}} > d_c \geq \overline{d}_c$) and scales linearly with pulse duration

until pulse durations $t_{\text{pulse}} < 1\text{ ms}$ are used. Below that threshold, the critical spacing levels off at $\overline{d}_c \sim 1\text{ nm}$.

The exceptionally small size of the features results from the nature of the writing process. The voltage-biased AFM tip produces large local electric fields ($E \sim V_{\text{tip}}/L$) across the $L = 1.2\text{-nm}$ -thick LaAlO_3 barrier. Tunnelling measurements carried out between the conducting AFM tip and the $\text{LaAlO}_3/\text{SrTiO}_3$ interface (Fig. 2b) show that for voltages $V_{\text{tip}} > V_t \sim 6\text{ V}$ the current I_{\perp} is governed by Fowler–Nordheim tunnelling between the tip and the interface. Tunnelling takes place over an area the radius of which may be estimated by assuming hertzian contact²³ to be $r_{\text{contact}} = 1.2\text{ nm}$. Writing at voltages smaller than V_t is possible, but not via direct tunnelling. Writing of conducting wires at, for example, $V_{\text{tip}} = 3\text{ V}$ is only achieved if a conducting path already exists to one of the electrodes (Fig. 1). Isolated conducting regions cannot be written with $V_{\text{tip}} < V_t$.

Because there is no strong anisotropy present in the SrTiO_3 or LaAlO_3 , the minimum lateral feature size is expected to be comparable to the scale for vertical confinement of the mobile electrons. Indeed, the smallest dot spacing observed is comparable to the observed thickness $\delta z = 2\text{ nm}$ for the quasi-two-dimensional

electron gas (q-2DEG) of a closely related system, LaTiO₃/SrTiO₃ (ref. 2). Using $\delta x = \delta z = 2$ nm and $l = 1$ μ m, we obtain a resistivity for the wires $\rho = \delta x \delta z / Gl = 2 \times 10^{-3}$ Ω cm, which is close to the Mott–Ioffe–Regel threshold.

We also carried out similar experiments on bare SrTiO₃, 2 unit cells of LaAlO₃ on SrTiO₃ and 4 unit cells of LaAlO₃ on SrTiO₃, the details of which are described in the Supplementary Information. Experiments show that only in the sample with 3 unit cell LaAlO₃ layer thickness¹⁰ conducting regions can be created and cleared at an insulating interface.

To provide insight into the electronic structure and stability of the metallic and insulating state of LaAlO₃/SrTiO₃, we carried out first-principles density functional theory calculations of LaAlO₃ films on SrTiO₃ substrates. These calculations do not consider possible correlation effects at the interface^{8,9}. Computational details are given in the Supplementary Information. Considering the experiment, an n-type (LaO/TiO₂) interface is used. The top surface of the LaAlO₃ is assumed to be clean and terminated with an AlO₂ layer. For 3-unit-cell-thick films, two structures are predicted to be stable. As shown in Supplementary Information, Fig. S1, the two structures differ by the presence of oxygen vacancies on the surface. The two structures are predicted to have dramatically different electrical properties. The ‘ideal’ film without vacancies (see Supplementary Information, Fig. S1a) is insulating. Removing oxygen ions from the LaAlO₃ surface layer (see Supplementary Information, Fig. S1b) accompanies the accumulation of mobile electrons at the interface.

The predicted behaviour of the two structures can be understood by examining the local density of states (LDOS), shown in Fig. 4, and the schematic band diagrams derived from the LDOS (see Supplementary Information, Fig. S2). The ideal film has a strong electric field in the LaAlO₃, but at 3 unit cells the heterostructure is insulating. With one extra LaAlO₃ unit cell the system becomes metallic¹⁰. The strong field is energetically expensive; by including oxygen vacancies at the LaAlO₃ surface, we find that the electric field can be reduced or completely compensated. Such LaAlO₃ oxygen vacancies contribute electrons to the conduction band, and the lowest-energy conduction band states are in the SrTiO₃ (see Supplementary Information, Fig. S2a). At a density of $n_v = 1/4$ vacancies per 1×1 surface cell, the formal charge of the surface has changed from $-1e$ for the ideal AlO₂ surface to $-e/2$ for the AlO_{1.75} surface. The $1/2$ electron per unit cell populates the SrTiO₃ conduction band on the opposite side of the LaAlO₃ film. In this scenario, the oxygen vacancies in the LaAlO₃ and conduction electrons of the SrTiO₃ together cancel the field in the LaAlO₃, as seen in Fig. 4 and Supplementary Information, Fig. S2b. The only metallic region in this system is the SrTiO₃ at the LaAlO₃/SrTiO₃ interface—the surface remains insulating.

In this model, switching between the two stable structures requires removing oxygen from the $n_v = 0$ surface and adding oxygen to the $n_v = 1/4$ surface. There are probably significant kinetic barriers to these processes, which the charged AFM tip may be able to overcome. Thus, without ruling out other mechanisms such as charging of trap states, this model suggests the possibility that a positively charged AFM tip ‘writes’ metallic wires at the interface by removing oxygen from the LaAlO₃ surface, and a negatively charged AFM tip ‘erases’ metallic regions by facilitating adsorption of oxygen or other anions. The theoretical calculations described here do not explain how oxygen might be removed or restored to the LaAlO₃ surface; they simply predict that a metal–insulator transition will result from this process. Further experimental and theoretical study is required to provide further insight into the physical mechanism that governs this effect.

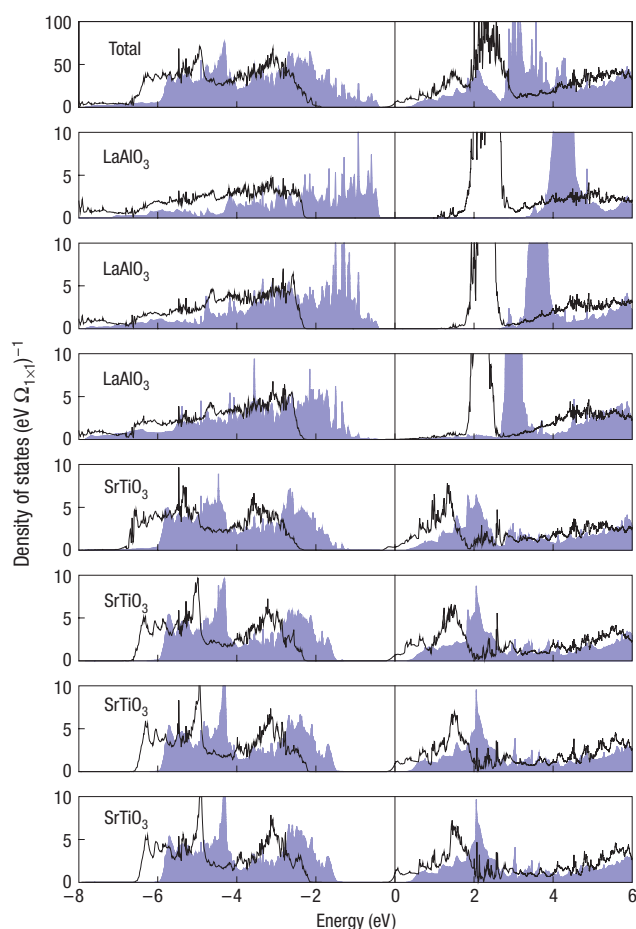


Figure 4 Calculated LDOS of LaAlO₃/SrTiO₃ for ‘ideal’ and reduced LaAlO₃ surfaces for each layer in the 3 unit cell LaAlO₃ film and for the first four unit cells of the SrTiO₃ substrate. The solid blue curve corresponds to the ‘ideal’ film, whereas the black curve corresponds to the film with surface oxygen vacancies. The ideal film is insulating and has a strong electric field in the LaAlO₃. With oxygen vacancies in the LaAlO₃ surface, the field is compensated, and 0.5 electrons per 1×1 unit cell enter the SrTiO₃ conduction states.

The ability to pattern reversibly high-mobility electron gases at nanoscale dimensions provides new ground to develop devices for ultrahigh-density information storage and processing. Integration with silicon-based devices is possible, as shown by reports of high-quality SrTiO₃/Si heterostructures produced by molecular-beam epitaxy²⁴.

References

- Schneider, C. W., Thiel, S., Hammerl, G., Richter, C. & Mannhart, J. Microlithography of electron gases formed at interfaces in oxide heterostructures. *Appl. Phys. Lett.* **89**, 122101 (2006).
- Ohtomo, A., Muller, D. A., Grazul, J. L. & Hwang, H. Y. Artificial charge-modulation in atomic-scale perovskite titanate superlattices. *Nature* **419**, 378–380 (2002).
- Ohtomo, A. & Hwang, H. Y. A high-mobility electron gas at the LaAlO₃/SrTiO₃ heterointerface. *Nature* **427**, 423–426 (2006).
- Ohtomo, A. & Hwang, H. Y. Corrigendum: A high-mobility electron gas at the LaAlO₃/SrTiO₃ heterointerface. *Nature* **441**, 120 (2006).
- Huijben, M. *et al.* Electronically coupled complementary interfaces between perovskite band insulators. *Nature Mater.* **5**, 556–560 (2006).
- Hotta, Y., Susaki, T. & Hwang, H. Y. Polar discontinuity doping of the LaVO₃/SrTiO₃ interface. *Phys. Rev. Lett.* **99**, 236805 (2007).
- Kalabukhov, A., Gunnarsson, R., Claesson, T. & Winkler, D. Electrical transport properties of polar heterointerface between KTaO₃ and SrTiO₃. Preprint at <<http://arxiv.org/abs/cond-mat/0704.1050>> (2007).
- Okamoto, S., Millis, A. J. & Spaldin, N. A. Lattice relaxation in oxide heterostructures: LaTiO₃/SrTiO₃ superlattices. *Phys. Rev. Lett.* **97**, 056802 (2006).

9. Pentcheva, R. & Pickett, W. E. Charge localization or itineracy at LaAlO₃/SrTiO₃ interfaces: Hole polarons, oxygen vacancies, and mobile electrons. *Phys. Rev. B* **74**, 035112 (2006).
10. Thiel, S., Hammerl, G., Schmehl, A., Schneider, C. W. & Mannhart, J. Tunable quasi-two-dimensional electron gases in oxide heterostructures. *Science* **313**, 1942–1945 (2006).
11. Ahn, C. H., Triscone, J.-M. & Mannhart, J. Electric field effect in correlated oxide systems. *Nature* **424**, 1015–1018 (2003).
12. Reyren, N. *et al.* Superconducting interfaces between insulating oxides. *Science* **317**, 1196–1199 (2007).
13. Haeni, J. H. *et al.* Room-temperature ferroelectricity in strained SrTiO₃. *Nature* **430**, 758–761 (2004).
14. Brinkman, A. *et al.* Magnetic effects at the interface between non-magnetic oxides. *Nature Mater.* **6**, 493–496 (2007).
15. Helmolt, R. v., Wecker, J., Holzapfel, B., Schultz, L. & Samwer, K. Giant negative magnetoresistance in perovskite like La_{2/3}Ba_{1/3}MnO_x ferromagnetic films. *Phys. Rev. Lett.* **71**, 2331–2333 (1993).
16. Levi, B. G. Interface between nonmagnetic insulators may be ferromagnetic and conducting. *Phys. Today* **60**, 23–27 (2007).
17. Eckstein, J. N. Oxide interfaces: Watch out for the lack of oxygen. *Nature Mater.* **6**, 473–474 (2007).
18. Schooley, J. F., Hosler, W. R. & Cohen, M. L. Superconductivity in semiconducting SrTiO₃. *Phys. Rev. Lett.* **12**, 474–475 (1964).
19. Siemons, W. *et al.* Origin of charge density at LaAlO₃ on SrTiO₃ heterointerfaces: Possibility of intrinsic doping. *Phys. Rev. Lett.* **98**, 196802 (2007).
20. Kalabukhov, A. *et al.* Effect of oxygen vacancies in the SrTiO₃ substrate on the electrical properties of the LaAlO₃/SrTiO₃ interface. *Phys. Rev. B* **75**, 121404 (2007).
21. Herranz, G. *et al.* High mobility in LaAlO₃/SrTiO₃ heterostructures: Origin, dimensionality, and perspectives. *Phys. Rev. Lett.* **98**, 216803 (2007).
22. Ahn, C. H. *et al.* Local, nonvolatile electronic writing of epitaxial Pb(Zr_{0.52}Ti_{0.48})O₃/SrRuO₃ heterostructures. *Science* **276**, 1100–1103 (1997).
23. Frammelsberger, W., Benstetter, G., Kiely, J. & Stamp, R. C-AFM-based thickness determination of thin and ultra-thin SiO₂ films by use of different conductive-coated probe tips. *Appl. Surf. Sci.* **253**, 3615–3626 (2007).
24. Li, H. *et al.* Two-dimensional growth of high-quality strontium titanate thin films on Si. *J. Appl. Phys.* **93**, 4521–4525 (2003).
25. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
26. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169–11186 (1996).
27. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **59**, 1758–1775 (1999).
28. Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **50**, 17953–17979 (1994).
29. Nakagawa, N., Hwang, H. Y. & Muller, D. A. Why some interfaces cannot be sharp. *Nature Mater.* **5**, 204–209 (2006).
30. Jenkins, S. J. Ternary half-metallics and related binary compounds: Stoichiometry, surface states, and spin. *Phys. Rev. B* **70**, 245401 (2004).

Acknowledgements

We gratefully acknowledge helpful interactions and discussions with T. Kopp and S. K. Streiffer. Computations were carried out at the DoD Major Shared Resource Centers. This work was supported by DARPA DAAD-19-01-1-0650, NSF DMR-0704022, the DFG (SFB 484), the EC (Nanoxide) and the ESF (THIOX). Correspondence and requests for materials should be addressed to J.L. Supplementary Information accompanies this paper on www.nature.com/naturematerials.