

Conducting interfaces between polar and non-polar insulating perovskites

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2008 J. Phys.: Condens. Matter 20 264012

(<http://iopscience.iop.org/0953-8984/20/26/264012>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 13:17

Please note that [terms and conditions apply](#).

TOPICAL REVIEW

Conducting interfaces between polar and non-polar insulating perovskites

S A Pauli and P R Willmott

Swiss Light Source, Paul Scherrer Institut, CH-5232 Villigen, Switzerland

E-mail: philip.willmott@psi.ch

Received 18 January 2008, in final form 22 February 2008

Published 9 June 2008

Online at stacks.iop.org/JPhysCM/20/264012**Abstract**

Two-dimensional electron gases in semiconductors have found use in applications such as optoelectronics, high-power radio-frequency and magnetoelectronic devices. The ability to grow heterostructures of oxides exhibiting similar effects is a significant step towards the fabrication of all-oxide devices. Here, we give an overview of recent studies of two-dimensional electron gases formed at the interface between polar and non-polar perovskites. We discuss the proposed explanations of the origin of the conductivity and properties of the ground state.

(Some figures in this article are in colour only in the electronic version)

Contents

1. Introduction	1
2. An electronic reconstruction	2
3. A high mobility electron gas	3
4. Possible explanations	4
4.1. Oxygen deficiency	4
4.2. A polar discontinuity	5
4.3. Lattice distortion	6
4.4. Cationic intermixing	6
5. Ground state	7
6. Conclusion	7
Acknowledgments	7
References	7

1. Introduction

Strongly correlated electron systems (SCESs) are a wide class of materials that show unusual electronic and magnetic properties. Many, if not most, transition metal oxides are SCESs, which, although chemically similar, exhibit the full gamut of electronic properties from band insulator, through Mott insulator, semiconductor, metal, to superconductor, and also many unusual magnetic properties such as colossal magnetoresistance, to name only a few examples [1–6].

The reason metal oxides, and in particular the family of perovskites, exhibit such a broad spectrum of physical

properties is because of the profound effect subtle structural changes, such as bond lengths and angles, have on the interplay between the valence electrons. The electronic structure of SCESs can neither be described by assuming nearly free electrons, nor by a completely ionic model. Rather, the situation is intermediate, involving a complex set of correlated electronic and magnetic phenomena, hence the term ‘strongly correlated electrons’. Such systems are difficult to model, because the balance between competing phenomena is easily shifted by small changes in the atomic structure, resulting in large physical effects [7, 8]. Hence, the possibility of engineering new and unexpected physical properties, and understanding the complexity of the underlying mechanisms represents a burgeoning field of research in modern condensed-matter physics.

A fundamental understanding of correlated electron effects in surfaces and interfaces is essential in the drive to fabricate future devices exploiting these effects. Indeed, this scientific endeavour is particularly important when one considers the prosaic fact that any electronic device must be coupled to the rest of the world via motion of electrons through an interface. Hence, in addition to the question of how the various unexpected and novel phases arise in bulk SCESs, one should ask what changes occur at their surfaces and interfaces.

The perovskite transition metal oxides have a general formula of ABO_3 , whereby the 12-fold coordinated A-site is mostly occupied by an alkaline-earth, whereas the six-fold

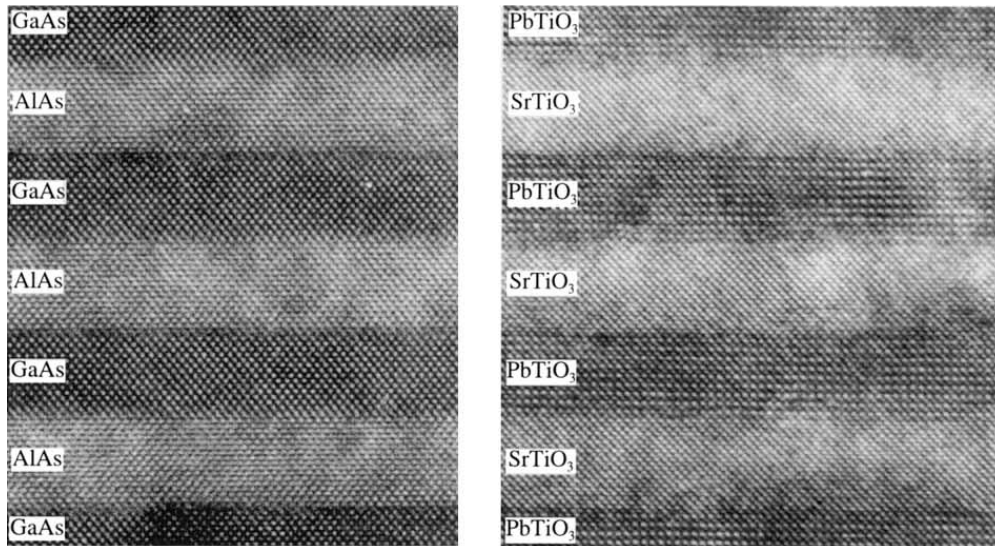


Figure 1. The figure shows a comparison of high-resolution transmission electron microscopy images of a semiconductor and an oxide heterostructure. The left image shows a GaAs/AlAs multilayer [9], while on the right a PbTiO₃/SrTiO₃ multilayer [10] is shown. Both have comparable thicknesses of the individual layers of 4 nm. Reprinted with permission from [10]. Copyright 1999, American Institute of Physics.

coordinated B-site contains a transition metal, a rare-earth-ion, or a group-III metal, surrounded by an octahedron of oxygen atoms. This structure can also be thought of as consisting of alternating AO and BO₂ atomic sublayers (ALs). Taking oxygen to have a formal valence of O²⁻, the A and B cations can assume values of A²⁺B⁴⁺, A³⁺B³⁺, etc. Hence those perovskites with the charge distribution A²⁺B⁴⁺O₃ contain formally neutral AO and BO₂ ALs (analogous with the (001) planes of the group IV semiconductors, such as Si or Ge), while A³⁺B³⁺O₃ structures (e.g. LaTiO₃ and LaAlO₃) have alternating AO⁺ and BO₂⁻ planes, just as the III-V or II-VI compound semiconductors, such as GaAs or CdTe, also have charged planes.

The crystallographic quality of heterostructures of thin oxide films, grown by pulsed laser deposition (PLD) [11], magnetron sputtering [12], or molecular beam epitaxy (MBE) [13] is nowadays comparable to that of semiconductor heterostructures, as shown in figure 1. While semiconductors are well understood and used in many technical applications, oxide electronics is still in its infancy. An important challenge of the next few years will be to discover which of the technical possibilities used in semiconductor science can be transferred to oxide structures.

In this review article, we will present the physical relationships between the atomic and electronic structures at the interface between two insulating materials, specifically between polar and non-polar materials. In the following section, we will discuss the so-called *electronic reconstruction*, arising at the interface between LaTiO₃ and SrTiO₃, both from a theoretical and an experimental point of view. In section 3 we concentrate on the interface between LaAlO₃ and SrTiO₃ and describe a quasi-two-dimensional electron gas (q2-DEG), which emerges in this heterostructure. In section 4, we discuss the different explanations advanced to explain the origin of the q2-DEG, while a discussion about the properties of its ground

state is reviewed in section 5. In the final section conclusions are drawn.

2. An electronic reconstruction

An interesting heterostructure was discovered by Ohtomo *et al* in 2002. They grew multilayers of SrTiO₃ and LaTiO₃, where the former is a band insulator with electrically neutral atomic planes and the latter is a Mott insulator with alternating charged atomic planes [14]. In SrTiO₃, titanium is tetravalent and has therefore an empty d-band, whereas in LaTiO₃, titanium is trivalent, and therefore has one d electron. Scanning transmission electron microscopy (STEM) images indicated an abrupt interface between the two materials, although the distribution of the titanium d-electrons, determined by electron energy loss spectroscopy (EELS) spectra was not abrupt but spread into the SrTiO₃. The central titanium site exhibited a bulk-like EELS spectrum only after five unit cells of LaTiO₃. These superlattices were metallic—the conductivity depends on the thickness of the LaTiO₃ interlayers and is about two thirds of the corresponding bulk La_xSr_{1-x}TiO₃ with the same stoichiometry [14]. Electrical conductivity measurements performed in 2004 by Shibuya *et al* confirmed metallic behaviour, with a lowest electrical resistivity of 200 μΩ cm at 300 K [15]. The temperature dependence of the resistivity could be described by the relation $\rho = \rho_0 + AT^2$ up to about 150 K, which indicates strong electron–electron interaction [16]. Photoemission studies observed a metallic Fermi edge [17].

This study inspired Okamoto and Millis to investigate these superlattices from a theoretical point of view [18–20]. The LaTiO₃/SrTiO₃ heterostructures are an ideal model to study the consequences of electronic charge spreading, i.e. *electronic reconstructions* alone. The two other key factors in correlated electron behaviour, namely changes in interaction strengths and bandwidths are minimized by the

chemical similarity and the near lattice match of these two materials. They calculated an electronic phase diagram as a function of the number of LaTiO_3 layers and the on-site interaction parameter, i.e. the ratio between the Hubbard term U and the hopping integral t . From this, they were able to determine the spatial variation of charge, spin and orbital densities for the relevant phases. They found that the near-interface region is metallic and ferromagnetic over a wide range of parameter space, whereas the bulk LaTiO_3 phase is insulating and antiferromagnetic. The transition region is about three layers wide, i.e. one needs at least seven layers of LaTiO_3 to recover bulk-like behaviour in the central region. Quasi-particle subbands exist near the Fermi edge, which have a non-negligible fraction of the total charge density, indicating a relatively robust metallic character. They found even in the presence of strong bulk correlations a finite mass renormalization. About the same width of the leakage of charge carriers into the SrTiO_3 was seen by Satpathy *et al* by local spin density approximation (LSDA and LSDA + U). The potential of the LaTiO_3 layer has a wedge-shape, forming an Airy-function delocalized electron distribution [21, 22]. In contrast to Okamoto and Millis, they found a paramagnetic transition region.

The effect of possible atomic rearrangements, however, was not considered. Because the titanium oxide octahedra are negatively charged, they should be more strongly attracted by the trivalent lanthanum than by the divalent strontium. In two further publications, the influence of such lattice relaxations was taken into account. Hamann *et al* performed density functional theory (DFT) calculations in the generalized gradient approximation (GGA), from which they could explain the charge spread of the titanium d-electrons by large polarization effects due to the different amounts of relaxations of the anions and cations in a model at finite temperature [24]. A similar ferroelectric-like distortion of the TiO_6 octahedra was found by Okamoto *et al* using local density approximation + Hubbard U calculations (LDA + U) [23]. The oxygen and the titanium ions were displaced relative to each other by about 0.15 \AA normal to the interface, which produces a local ionic moment that screens the Coulomb field created by the substitution of Sr^{2+} by La^{3+} ions. This leads to an increase of the Ti–Ti distance by about 0.08 \AA , as can be seen in figure 2(a). The screening caused by the lattice relaxation reduces the charge density on the central titanium atom and produces a charge spread into the SrTiO_3 , as shown in figure 2(b). The relaxations also dramatically changed the electronic phase diagram and formed a novel symmetry-breaking-induced ordering of the xy orbitals, which occurs neither in bulk LaTiO_3 , nor in the unrelaxed case for this superstructure.

3. A high mobility electron gas

A similar behaviour was found between two band-insulating materials by Ohtomo and Hwang, who reported on the formation of a high mobility, quasi-two-dimensional electron gas (q2-DEG) at the interface between LaAlO_3 and SrTiO_3 . They found an extremely high carrier mobility,

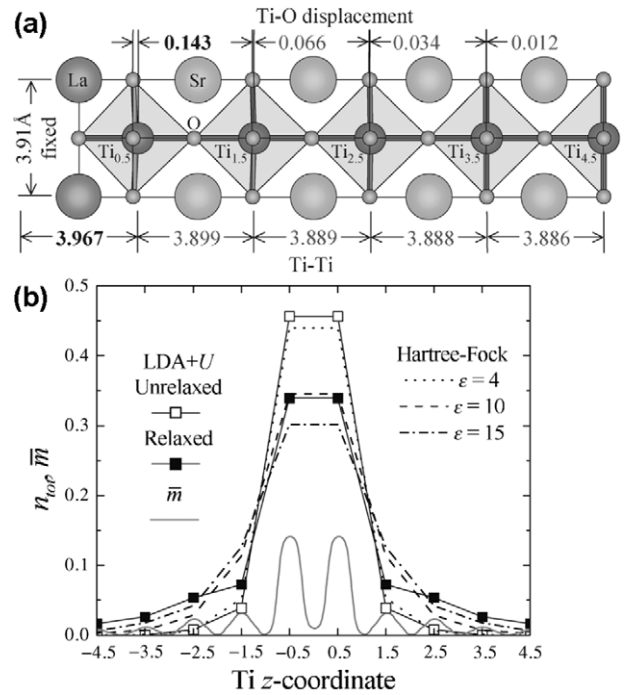


Figure 2. (a) The calculated optimized lattice structures of the $[\text{LaTiO}_3]_1/[\text{SrTiO}_3]_8$ superstructure. (b) The charge density for the same superstructure for both the relaxed and unrelaxed case. Reprinted figure with permission from [23]. Copyright 2006 by the American Physical Society.

up to $10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (which, they noted, seemed to be unphysically high), with quantized magnetoresistance peaks, whereby the peak order number was inversely proportional to the magnetic field [25]. If we consider heteroepitaxial film growth on a single-layer terminated perovskite substrate, two different interfaces can arise, as illustrated in figure 3: if the SrTiO_3 is terminated by a TiO_2 layer, LaAlO_3 starts growing with an LaO layer, whereas LaAlO_3 begins with the AlO_2 layer if the top SrTiO_3 layer is SrO . In the ionic limit, the SrO and TiO_2 layers are charge-neutral, whereas the LaO and AlO_2 layers are positively and negatively charged, respectively, and have a net charge of one layer of $\pm\sigma$.

This alternating layer charge induces an electric dipole, which must be compensated for an ideal and abrupt planar interface. Otherwise, the electric potential across the film layer increases linearly with thickness, which rapidly results in an unphysical surface potential. In order to avoid such a polar catastrophe, Noguera showed that the surface and interface layers have to have a net charge of $\sigma/2$ [26]. Such a compensation in $\text{AlO}_2/\text{LaO}_2/\text{TiO}_2$ interfaces could be realized by a mixed valence state of titanium (one half Ti^{3+} , one half Ti^{4+}). So that on average, there is half an electron extra per unit cell, which results in an ‘n-type’-like interface. In the case of an $\text{AlO}_2/\text{SrO}/\text{TiO}_2$ interface, the only possible way of compensating is by invoking oxygen vacancies (p-type), since none of the cations can assume still higher valence states. Interestingly, the n-type interface was shown to be conducting, while the p-type is insulating.

Ohtomo and Hwang measured the Hall resistance of the samples in a typical six-probe Hall bar geometry with contacts

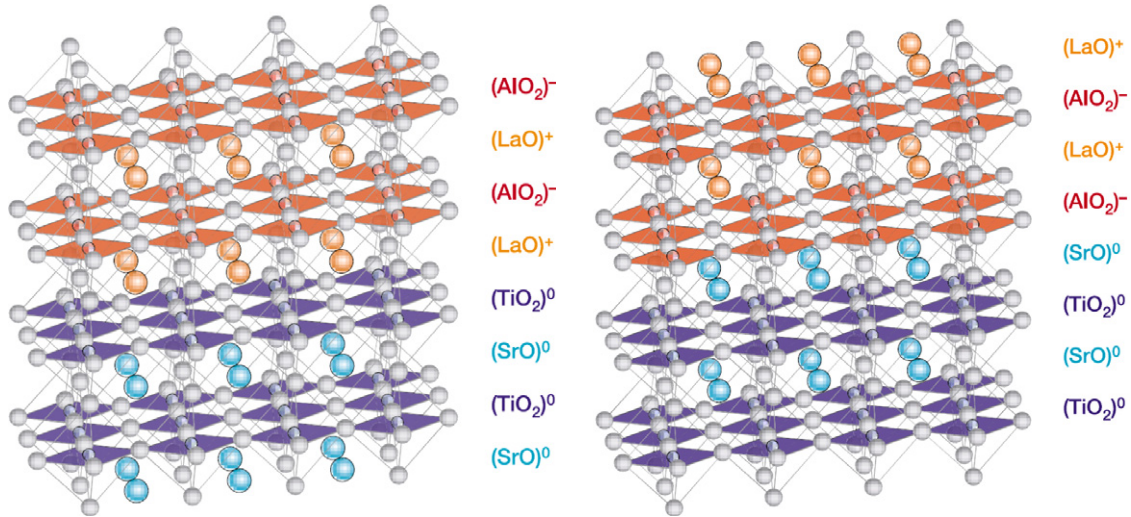


Figure 3. Schematics of two different possible interfaces of the $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructure. The left and right images show the n-type structure with a TiO_2/LaO interface, and the p-type structure with SrO/AlO_2 interface, respectively. Reprinted by permission from Macmillan Publishers Ltd: *Nature* [25], copyright 2004.

Table 1. Summary of the PLD growth conditions, i.e. the oxygen partial pressure, the temperature, laser fluence, post-growth annealing and the measured sheet carrier densities.

p_{O_2} (mbar)	T ($^\circ\text{C}$)	Laser fluence (J cm^{-2})	O_2 post-annealing	n_s (cm^{-2})	Reference
10^{-4} – 10^{-6}	800	1	—	3×10^{14} – 10^{17}	[25]
10^{-5}	750	3	4 h, 550°C	5×10^{14}	[31]
10^{-6}	750	n.g. ^a	—	n.g.	[32]
3×10^{-5}	850	1.3	—	1.8×10^{14}	[33]
2 – 6×10^{-5}	770	n.g.	2.5 h, 600°C	10^{13}	[34–36]
10^{-6}	800	2	— ^b	10^{16} – 10^{17}	[37]
10^{-5} – 10^{-6}	815	~ 1	—	2×10^{16}	[29, 30]
10^{-3} – 10^{-6}	750	n.g.	—	n.g.	[38]
1.0 – 2.5×10^{-3}	850	n.g.	—	n.g.	[39]
5×10^{-6}	770	1	—	n.g.	[40]

^a Not given in reference.

^b In some cases, the samples were simply allowed to cool in 500 mbar O_2 .

penetrating to the interface. Interpreting their experimental result as being due to free charge carrier density would imply $n = 10^{17} \text{ cm}^{-2}$. This should be compared to $3.3 \times 10^{14} \text{ cm}^{-2}$ for half an electron per unit cell, as would be expected by a simple electronic reconstruction. Indeed, in this first report, Ohtomo and Hwang noted that the measured conductivity was unphysically high. Their work attracted a worldwide concerted effort to explain the conductivity of the interface, but also to determine the ground state of the electron gas. In the next section, we will summarize the work performed to explain the conductance from both a theoretical and an experimental point of view.

4. Possible explanations

4.1. Oxygen deficiency

Ohtomo and Hwang could not exclude the possibility of oxygen vacancies within their sample [25]. It is well known that even for a small oxygen deficiency, $\text{SrTiO}_{3-\delta}$

becomes semiconducting and then metallic, and that the mobility of the charge carriers is high even for high charge carrier concentrations [27]. Siemons *et al* confirmed the resistivity and mobility measurements. Their ultraviolet photoelectron spectroscopy (UPS) data also indicated electron states extending up to the Fermi energy [28–30]. Their growth conditions were similar to those of Ohtomo and Hwang—the oxygen background pressure was about $1.33 \times 10^{-4} \text{ Pa}$. Subsequent oxygen annealing lowered the density of states at the surface. In addition, they found that the repetition rate of the pulsed laser had an influence on the electronic properties. Both these results underline the influence of subtle changes in the growth conditions on the structure. All the different growth conditions and sheet carrier densities of the various studies mentioned in this paper are summarized in table 1.

Since the number of states was lowered when the sample was oxidized, they concluded that the anomalously high conductivity is due to the introduction of oxygen vacancies. Since the initial SrTiO_3 was not conducting at all and had no oxygen vacancies, it was proposed that they were introduced

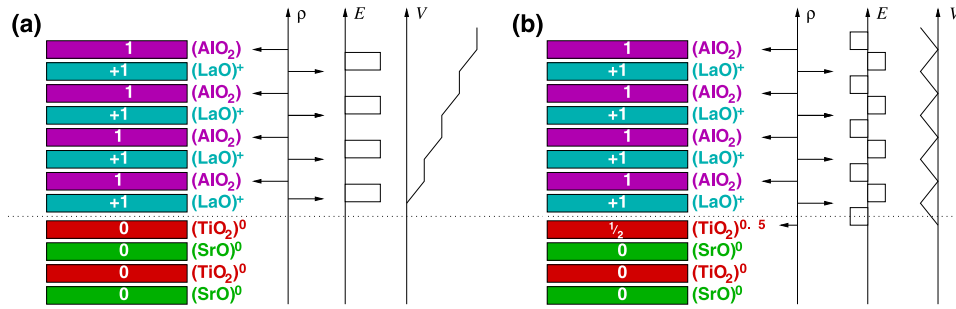


Figure 4. (a) The polar catastrophe: the electric potential induced by the alternating charged layers increases with each layer of LaAlO_3 . In (b), divergence is avoided by transfer of half an electron per unit cell in the top titanium layer.

by the PLD process, whereby the energetic particles from the ablation plume impinging on the surface sputter off the oxygen. They further assumed that the vacancies were confined to a thin layer near the interface, whereas the electrons are separated from the dopants and spread exponentially deep into the substrate.

Kalabukhov *et al* compared photoluminescence and cathodoluminescence measurements of three different systems, i.e. of SrTiO_3 with oxygen vacancies induced by Ar-bombardment, of LaAlO_3 films grown on SrTiO_3 substrates under typical growth conditions and of SrTiO_3 substrates subjected to the same typical growth conditions and times, but without actual LaAlO_3 film growth [37]. All three sample types showed very similar behaviour in conductivity and optical properties. Subsequent oxygen annealing of the samples always increased the resistivity.

Herranz *et al* measured the resistivity as a function of an applied magnetic field, both perpendicular and parallel to the current, and found Shubnikov–de Haas (SdH) oscillations at $T < 4$ K and magnetic fields $B \geq 6$ T [38]. The SdH frequencies in the magnetoresistance were the same for both orientations for the magnetic field, which suggests a uniform 3D character of the electronic system—the calculated thickness of the conducting layer in their results is strikingly close to the substrate thickness. Indeed, they observed similar mobilities and resistivities for homoepitaxially grown oxygen-deficient $\text{SrTiO}_{3-\delta}$ and Co-doped $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ samples from earlier studies [41].

These studies demonstrate that there is no doubt that oxygen vacancies exist to a lesser or greater extent, depending, above all, on the background pressure of oxygen during film growth and that they affect the conductivity. Film growth performed at low oxygen pressure, i.e. below 10^{-3} Pa, results in high oxygen vacancy concentrations, which can well describe the high mobility and conductivity of the samples. But, if the growth is performed under higher oxygen pressure, the films are still conducting, albeit with conductivities which are two to three orders of magnitude lower. The number of charge carriers lies in the region of the intrinsic charge carrier limit of $3.2 \times 10^{-14} \text{ cm}^{-2}$. Brinkman *et al* have shown that, if the density of charge carriers, induced by oxygen vacancies n_{ox} falls below this region, the intrinsic charge carriers play a major role [39]. Crucially, however, those interfaces involving the SrO/AlO_2 sublayers were always insulating. We discuss this important result now.

4.2. A polar discontinuity

If the conductivity does not vanish when there are no or very few oxygen vacancies, there must be another reason for the conducting interface. Ohtomo and Hwang explained their discovery by an electronic reconstruction due to a polar discontinuity at the interface [25], i.e. the alternating positive and negative atomic layers of LaAlO_3 lead to a nonzero dipole moment. As mentioned in section 3, this has to be compensated at the surface [26, 42]. Such an interface is shown in figure 4. Although an anomalously high mobility and charge carrier density can be explained by oxygen vacancies, this electronic reconstruction can be the underlying cause of conductivity at the interface for samples grown at higher oxygen pressures. Discontinuities between polar and non-polar materials influence the interface, because there must be a compensation of the electrical dipole here. Materials with a considerable polar character, however, introduce a larger energy cost for atomically abrupt interfaces (see figure 4(a)). This can lead to atomic structural changes in the interface region. For example, it is known for traditional semiconductors that growing polar films on non-polar materials (GaAs on Ge or Si) can cause significant interface roughening, unless the composition transition is graded to ensure there is no net formal interface charge. This grading results in a microscopically rough interface and, in many cases, also a measurable electrical band offset [43–45].

However, Nakagawa *et al* proposed in 2006: ‘If the electrons can move, the atoms do not have to’ [31]. Importantly, titanium can be either trivalent or tetravalent. In other words, in the trivalent state, it contains one 3d electron. If there is an electronic reconstruction, the titanium in the TiO_2 atomic layer between $(\text{LaO})^+$ and SrO is in a mixed valence state. If we assume a nominal average charge of +3.5 (i.e. transfer of half a layer charge into the TiO_2 AL) for this interfacial titanium, the polar catastrophe is avoided, as can be seen in figure 4(b).

Thiel *et al* proposed that a minimal electrical potential must build up in order to induce electron transfer [34, 35]: The electrical potential V_{stack} , resulting from stacking the polar $(\text{LaO})^+$ and $(\text{AlO}_2)^-$ on top of the SrTiO_3 substrate, diverges with the layer thickness—or, in other words, with the number of deposited layers of LaAlO_3 . A reconfiguration of ‘mobile’ electrons occurs only if the energy difference between the state of mobile electrons E_{mobile} and the initial configuration E_0 is

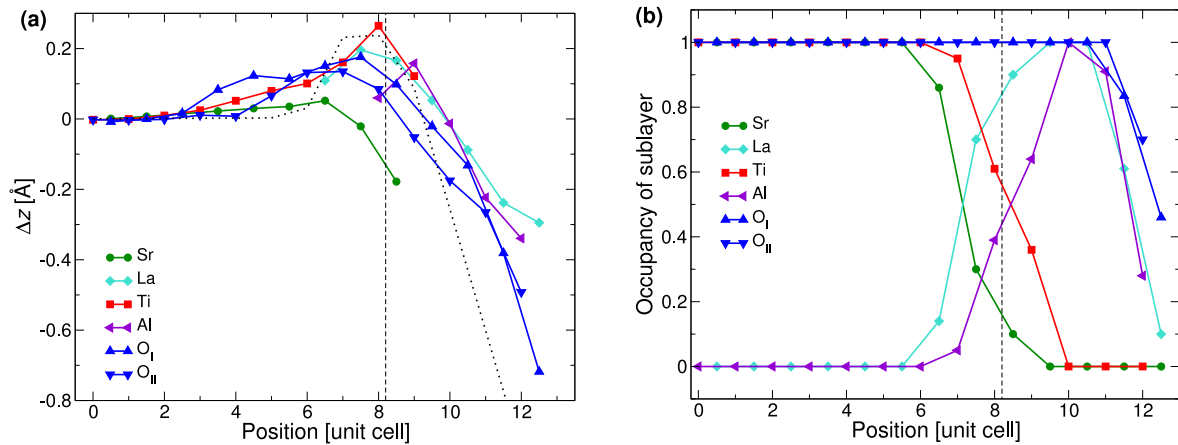


Figure 5. (a) Cumulative out-of-plane lattice deviation from a bulk SrTiO₃ reference frame of a five-monolayer LaAlO₃ on SrTiO₃ heterostructure. (b) Interfacial occupation of the different ions in the heterostructure [40].

smaller than the electrical potential, i.e. $E_{\text{mobile}} - E_0 = \Delta E < V_{\text{stack}} = nV_{\text{u.c.}}$, where $V_{\text{u.c.}}$ is the potential build up per unit cell thickness. A lower limit of the number of unit cells required to induce the electronic reconstruction would then be of the order $n_c = \Delta E / V_{\text{u.c.}}$. It was found experimentally that the lower limit was $n_c =$ four unit cells of LaAlO₃ [34].

Although most research has been performed on single interfaces, Huijben *et al* investigated the influence of the p-type (AlO₂/SrO) interface on the n-type (LaO/TiO₂) interface in an early study [33]. They varied the number of LaAlO₃ layers buried within SrTiO₃ and *vice versa*. For separation distances of less than six monolayers they determined an increase in sheet resistivity, independent of the heterostructure type. This thickness matches well with the minimal size needed to recover bulk-like behaviour in the LaTiO₃/SrTiO₃ system described above. The sheet carrier density for a large separation between the interfaces was approximately $1.8 \times 10^{14} \text{ cm}^{-2}$, which corresponds to about a quarter of an electron per unit cell.

According to a theoretical study by Park *et al*, both electron- and hole-doped interfaces should be metallic [46]. However, the influence of oxygen vacancies in the case of an n-type interface only introduces further electrons, i.e. n-type charge carriers, and conductivity is increased. In the case of a p-type interface, the charge carriers are holes. The introduction of oxygen vacancies, and therefore electrons, compensate the holes present at the interface.

4.3. Lattice distortion

Since the unit cell of SrTiO₃ is slightly larger than that of LaAlO₃, one might expect a decrease of the out-of-plane lattice constant for LaAlO₃ films heteroepitaxially (i.e. pseudomorphically) grown on SrTiO₃. In fact, a dilation at the interface was observed by Maurice *et al*, using high-resolution transmission electron microscopy (HRTEM) [32]. They argued that a Jahn–Teller like distortion is the reason for the elongation, which minimizes the electron energy: the two atomic sublayers LaO and TiO₂ across the interface form a unit cell of LaTiO₃, which has a larger lattice constant (by 0.065 Å for pseudocubic bulk unit cells). The d_{xz} and d_{yz} orbitals of the

t_{2g} states are therefore lowered in energy compared to that for the d_{xy} state. Implicit in this explanation is the trivalent nature of the titanium ion in this single LaTiO₃ monolayer.

Vonk *et al* measured the initial structure of LaAlO₃ on SrTiO₃ films for a deposition of less than one monolayer, using surface x-ray diffraction (SXR) [47]. For a half occupied first monolayer of LaAlO₃, the displacements are qualitatively similar to those in the HRTEM results. A comprehensive SXR study was performed by Willmott *et al* [40], who studied a five-monolayer thick film. This study also confirmed the interfacial dilation, which can be seen in figure 5(a). They explained the lattice deviations by simple ionic considerations of intermixed cations at the interface, discussed in more detail below.

4.4. Cationic intermixing

So far, we have considered the interface as abrupt and atomically perfect. However, Nakagawa *et al* found that the roughness of the conducting n-type interface is approximately 1.9 unit cells. The insulating p-type interface roughness, however, is only 0.77 unit cells [31]. This roughening, or the exchange of strontium by lanthanum, reduces the dipole at the interface. In the p-type interface, there is no delocalized screening electron, and any dipole can be compensated by oxygen vacancies, so there is no need for cationic intermixing.

In their SXR study, Willmott *et al* could confirm this interfacial roughening [40]. In fact the changeover from strontium to lanthanum occurs not 0.5 unit cells deep, but in fact 1.5 unit cells deeper in the structure than the one from titanium to aluminium (see the two crossover points in figure 5(b)). They argue that the thus formed (La, Sr)TiO₃, which is known to be metallic for a broad compositional range, is the origin of the conductivity of the interface.

In a very recent work, Fitting Kourkoutis *et al* studied the heterostructures of LaVO₃—a Mott-insulator—and SrTiO₃ [48]. LaVO₃ also consists of alternately charged atomic layers. The interface has a roughness of about 1.77 unit cells, which is very similar to that found in interfaces with LaAlO₃. They explained it by segregation of strontium into LaVO₃.

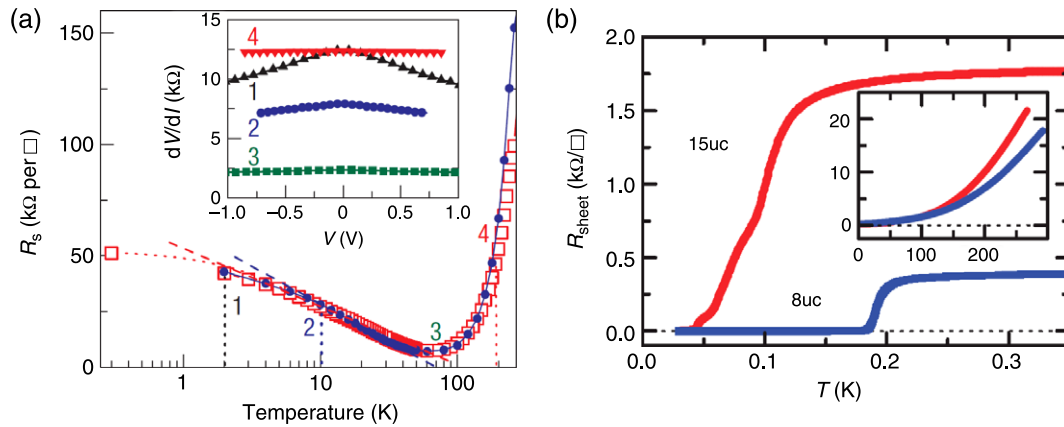


Figure 6. (a) Logarithmic dependence of the increase of resistivity towards lower temperatures, forming a ferromagnetic ground state. Inset: four-point differential resistance as a function of applied voltage, at a constant temperature of 2, 10, 50 and 180 K (curves 1–4, respectively). Reprinted by permission from Macmillan Publishers Ltd: *Nature Materials* [39], copyright 2007. (b) Transport measurements of the superconducting ground state: sheet resistance versus temperature. From [36]. Reprinted with permission from AAAS.

In another recent publication, Hotta *et al* investigated the transport properties of these heterostructures [49]. Interestingly, in the (001)-direction the n-type interface is conducting, whereas the p-type is insulating, i.e. the same as for $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces. Furthermore, they also inspected the interface in the (110)-direction, where both SrTiO_3 and LaVO_3 consists of alternately charged atomic layers, formally of ± 4 elementary charges per surface net cell. This structure has no polar discontinuity and is also insulating.

5. Ground state

Pentcheva and Pickett predicted a ferromagnetic behaviour of the interfacial d-electrons at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface [50]. Okamoto and Millis also predicted a highly polarized ferromagnetic ground state at the interfaces in similar $\text{LaTiO}_3/\text{SrTiO}_3$ superlattices. In both papers, the conduction electrons are localized at the Ti-lattice site. Okamoto predicts that the screening due to the lattice relaxation produces a long ‘tail’ in the charge distribution into the SrTiO_3 [23].

The growth conditions (i.e. temperature and ambient oxygen pressure) not only govern the origin of the charge carriers, but also influence the ground state of the material. There is an ongoing debate regarding the ground state of the electron. Brinkman *et al* found a minimum in resistivity at a finite temperature (see figure 6(a)). The sheet resistance could be described by $R_S = a \ln(T/T_{\text{eff}}) + bT^2 + cT^5$, where the potential terms come from electron–electron and electron–phonon scattering and T_{eff} can be interpreted as the Kondo temperature [39]. They further observed a large negative magnetoresistance effect, which is independent of the direction of the magnetic field. This indicates that the magnetoresistance is caused by the spins of localized electrons and not by orbital effects.

Brinkman *et al* grew their films at higher temperatures and oxygen pressures ($p \geq 10^{-4}$ mbar, $T = 850^\circ\text{C}$) than Reyren *et al*, who found a superconducting ground state, with a critical temperature as high as $T_c = 200$ mK [36]. The phase transition of the electron gas to its superconducting state can be

described by a two-dimensional electron system, undergoing a Berezinskii–Kosterlitz–Thouless transition [51, 52]. They set an upper limit of the superconducting sheet thickness of 10 nm, whereas the coherence length of the Cooper pairs is about 70 nm.

6. Conclusion

In conclusion, the meteoric progress in the fundamental understanding of thin film growth and atomic engineering of polar interfaces in oxide heterostructures over the last four to five years has laid the bedrock for the future fabrication of integrated electronic devices using these exceptionally adaptable materials. It is expected that the effect of metallicity at the interface between insulators, a wonderfully illustrative example of how subtle changes in the structure of these systems can lead to fundamental changes in physical properties, will play an important role in the future success of this technology.

Acknowledgments

The financial support of the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung is gratefully acknowledged.

References

- [1] Bednorz J G and Müller K A 1986 Possible high T_c superconductivity in the Ba–La–Cu–O system *Z. Phys. B* **64** 189
- [2] Mott N F 1990 *Metal–insulator Transitions* 2nd edn (London: Taylor and Francis)
- [3] Jin S, Tiefel T H, McCormack M, Fastnacht R A, Ramesh R and Chen L H 1994 Thousandfold change in resistivity in magnetoresistive La–Ca–Mn–O films *Science* **264** 413
- [4] Salamon M B and Jaime M 2001 The physics of manganites: structure and transport *Rev. Mod. Phys.* **73** 583

- [5] Ahn C H, Rabe K M and Triscone J-M 2004 Ferroelectricity at the nanoscale: local polarization in oxide thin films and heterostructures *Science* **303** 488
- [6] Fong D D, Stephenson G B, Streiffer S K, Eastman J A, Auciello O, Fuoss P H and Thompson C 2004 Ferroelectricity in ultrathin perovskite films *Science* **304** 1650
- [7] Tokura Y 2003 Correlated-electron physics in transition-metal oxides *Phys. Today* **56** (July) 50
- [8] Inoue I H 2005 Electrostatic carrier doping to perovskite transition-metal oxides *Semicond. Sci. Technol.* **20** S112
- [9] Gutakovskii A K, Fedina L I and Aseev A L 1995 High resolution electron microscopy of semiconductor interfaces *Phys. Status Solidi a* **150** 127
- [10] Jiang J C, Pan X Q, Tian W, Theis C D and Schlom D G 1999 Abrupt PbTiO₃/SrTiO₃ superlattices grown by reactive molecular beam epitaxy *Appl. Phys. Lett.* **74** 2851
- [11] Willmott P R and Huber J R 2000 Pulsed laser vaporization and deposition *Rev. Mod. Phys.* **72** 315
- [12] Willmott P R 2004 Deposition of complex multielemental thin films *Prog. Surf. Sci.* **76** 163
- [13] Chambers S A 2000 Epitaxial growth and properties of thin film oxides *Surf. Sci. Rep.* **39** 105
- [14] Ohtomo A, Muller D A, Grazul J L and Hwang H Y 2002 Artificial charge-modulation in atomic-scale perovskite titanate superlattices *Nature* **419** 378
- [15] Shibuya K, Ohnishi T, Kawasaki M, Koinuma H and Lippmaa M 2004 Metallic LaTiO₃/SrTiO₃ superlattice films on the SrTiO₃ (100) surface *Japan. J. Appl. Phys.* **43** L1178
- [16] Tokura Y, Taguchi Y, Okada Y, Fujishima Y, Arima T, Kumagai K and Iye Y 1993 Filling dependence of electronic properties on the verge of metal–Mott-insulator transition in Sr_{1-x}La_xTiO₃ *Phys. Rev. Lett.* **70** 2126
- [17] Takizawa M *et al* 2006 Photoemission from buried interfaces in SrTiO₃/LaTiO₃ superlattices *Phys. Rev. Lett.* **97** 057601
- [18] Okamoto S and Millis A J 2004 Electronic reconstruction at an interface between a Mott insulator and a band insulator *Nature* **428** 630
- [19] Okamoto S and Millis A J 2004 Theory of Mott insulator–band insulator heterostructures *Phys. Rev. B* **70** 075101
- [20] Okamoto S and Millis A J 2004 Spatial inhomogeneity and strong correlation physics: a dynamical mean-field study of a model Mott-insulator–band-insulator heterostructure *Phys. Rev. B* **70** 241104
- [21] Popovic Z S and Satpathy S 2005 Wedge-shaped potential and Airy-function electron localization in oxide superlattices *Phys. Rev. Lett.* **94** 176805
- [22] Thulasi S and Satpathy S 2006 Jellium model of the two-dimensional Airy electron gas at the perovskite titanate interface *Phys. Rev. B* **73** 125307
- [23] Okamoto S, Millis A J and Spaldin N A 2006 Lattice relaxation in oxide heterostructures: LaTiO₃/SrTiO₃ superlattices *Phys. Rev. Lett.* **97** 056802
- [24] Hamann D R, Muller D A and Hwang H Y 2006 Lattice-polarization effects on electron-gas charge densities in ionic superlattices *Phys. Rev. B* **73** 195403
- [25] Ohtomo A and Hwang H Y 2004 A high-mobility electron gas at the LaAlO₃/SrTiO₃ heterointerface *Nature* **427** 423
- [26] Noguera C 2000 Polar oxide surfaces *J. Phys.: Condens. Matter* **12** R367
- [27] Tufte O N and Chapman P W 1967 Electron mobility in semiconducting strontium titanate *Phys. Rev.* **155** 796
- [28] Siemons W, Koster G, Yamamoto H, Harrison W A, Geballe T H, Blank D H A and Beasley M R 2006 Origin of the unusual transport properties observed at hetero-interfaces of LaAlO₃ on SrTiO₃ *Preprint cond-mat/0603598*
- [29] Siemons W, Koster G, Yamamoto H, Harrison W A, Lucovsky G, Geballe T H, Blank D H A and Beasley M R 2007 Origin of charge density at LaAlO₃ on SrTiO₃ heterointerfaces: possibility of intrinsic doping *Phys. Rev. Lett.* **98** 196802
- [30] Siemons W, Koster G, Yamamoto H, Geballe T H, Blank D H A and Beasley M R 2007 Experimental investigation of electronic properties of buried heterointerfaces of LaAlO₃ on SrTiO₃ *Phys. Rev. B* **76** 155111
- [31] Nakagawa N, Hwang H Y and Muller D A 2006 Why some interfaces cannot be sharp *Nat. Mater.* **5** 204
- [32] Maurice J-L, Carrétéro C, Casanove M-J, Bouzouhouane K, Guyard S, Larquet É and Contour J-P 2006 Electronic conductivity and structural distortion at the interface between insulators SrTiO₃ and LaAlO₃ *Phys. Status Solidi a* **203** 2209
- [33] Huijben M, Rijnder G, Blank D H A, Bals S, Van Aert S, Verbeeck J, Van Tendeloo G, Brinkman A and Hilgenkamp H 2006 Electronically coupled complementary interfaces between perovskite band insulators *Nat. Mater.* **5** 556
- [34] Thiel S, Hammerl G, Schmehl A, Schneider C W and Mannhart J 2006 Tunable quasi-two-dimensional electron gases in oxide heterostructures *Science* **313** 1942
- [35] Schneider C W, Thiel S, Hammerl G, Richter C and Mannhart J 2006 Microlithography of electron gases formed at interfaces in oxide heterostructures *Appl. Phys. Lett.* **89** 122101
- [36] Reyren N *et al* 2007 Superconducting interfaces between insulating oxides *Science* **317** 1196
- [37] Kalabukhov A, Gunnarsson R, Börjesson J, Olsson E, Claesson T and Winkler D 2007 Effect of oxygen vacancies in the SrTiO₃ substrate on the electrical properties of the LaAlO₃/SrTiO₃ interface *Phys. Rev. B* **75** 121404(R)
- [38] Herranz G *et al* 2007 High mobility in LaAlO₃/SrTiO₃ heterostructures: origin, dimensionality, and perspectives *Phys. Rev. Lett.* **98** 216803
- [39] Brinkman A, Huijben M, van Zalk M, Huijben J, Zeitler U, Maan J C, van der Wiel W G, Rijnders G, Blank D H A and Hilgenkamp H 2007 Magnetic effects at the interface between non-magnetic oxides *Nat. Mater.* **6** 493
- [40] Willmott P R *et al* 2007 Structural basis for the conducting interface between LaAlO₃ and SrTiO₃ *Phys. Rev. Lett.* **99** 155502
- [41] Herranz G *et al* 2006 Full oxide heterostructure combining a high-*T_c* diluted ferromagnet with a high-mobility conductor *Phys. Rev. B* **73** 064403
- [42] Tasker P W 1979 The stability of ionic crystal surfaces *J. Phys. C: Solid State Phys.* **12** 4977
- [43] Harrison W A, Kraut E A, Waldrop J R and Grant R W 1978 Polar heterojunction interfaces *Phys. Rev. B* **18** 4402
- [44] Baraff G A, Appelbaum J A and Hamann D R 1977 Self-consistent calculation of the electronic structure at an abrupt GaAs–Ge interface *Phys. Rev. Lett.* **38** 237
- [45] Kroemer H 1987 Polar-on-nonpolar epitaxy *J. Cryst. Growth* **81** 193
- [46] Park M S, Rhim S H and Freeman A J 2006 Charge compensation and mixed valency in LaAlO₃/SrTiO₃ heterointerfaces studied by the FLAPW method *Phys. Rev. B* **74** 205416
- [47] Vonk V, Huijben M, Driessen K J I, Tinnemans P, Brinkman A, Harkema S and Graafsma H 2007 Interface structure of SrTiO₃/LaAlO₃ at elevated temperatures studied *in situ* by synchrotron x rays *Phys. Rev. B* **75** 235417
- [48] Fitting Kourkoutis L, Muller D A, Hotta Y and Hwang H Y 2007 Assymmetric interface profiles in LaVO₃/SrTiO₃ heterostructures grown by pulsed laser deposition *Appl. Phys. Lett.* **91** 161301

- [49] Hotta Y, Susaki T and Hwang H Y 2007 Polar discontinuity doping of the $\text{LaVO}_3/\text{SrTiO}_3$ interface *Phys. Rev. Lett.* **99** 236805
- [50] Pentcheva R and Pickett W E 2006 Charge localization or itineracy at $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces: hole polarons, oxygen vacancies, and mobile electrons *Phys. Rev. B* **74** 035112
- [51] Berezinskii V L 1972 Destruction of long-range order in one-dimensional and two-dimensional systems possessing a continuous symmetry group. ii. Quantum systems *Sov. Phys.—JETP* **34** 610
- [52] Kosterlitz J M and Thouless D J 1972 Long range order and metastability in two-dimensional solids and superfluids *J. Phys. C: Solid State Phys.* **5** L124