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Progress and Perspectives of Atomically Engineered Perovskite Oxide Interfaces for Electronics and Electrocatalysts

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Abstract:
The two-dimensional electron gases (2DEGs) at the surfaces and interfaces of SrTiO₃-based homo- and hetero-structures provide new opportunities for electronics and spintronics. Herein, the recent progresses in the creation of advanced material systems of conducting oxide interfaces with engineered electronic reconstructions and redox reactions, as well as their characterization by a non-destructive resonant X-ray reflectivity technique, are summarized. Moreover, the development of modulation-doped high-mobility oxide 2DEGs and the magnetic-proximity-induced spin-polarized 2DEGs at oxide interfaces are also discussed. Finally, the perspectives on design of conducting oxide interfaces for a new generation of quantum devices and mixed electronic and ionic conducting electrocatalysts are addressed. Atomically-engineered oxide interfaces will represent a unique family of quantum materials for future information and energy technologies.
1. Introduction

Among the technological problems that require attention today are that silicon electronics has reached fundamental scaling limits and that a secure society transition from fossil fuels to renewable energy sources is required. Solutions to both of these challenges require breakthroughs in material science. Thanks to the strong interplay between the charge, spin, orbital and lattice degrees of freedom, the interfaces and electrochemical interfaces of transitional metal oxides, particularly perovskite oxides\textsuperscript{1-3}, present the richest variety of emergent states, including colossal magnetoresistance, high-temperature superconductivity, high mobility two-dimensional electron gases (2DEGs) and enhanced oxygen surface exchange as well as the rate of oxygen redox reactions (ORR), just to name a few. These extraordinary properties provide new opportunities for electronics and electrocatalysts\textsuperscript{1-3}.

Notably, the continuous development in thin film epitaxial growth and characterization of complex oxides with atomic precision over the past 30 years, particularly the monolayer-by-monolayer design and control of perovskite oxide thin films\textsuperscript{4,5} and the atomic and element-specific characterization of the structural and electronic structure of oxide interfaces,\textsuperscript{6,7} has significantly improved our ability and understanding of oxide interfaces for electronics. A particular significant development is the emergence of the electronic conduction at the oxide interfaces between two band insulators, one of which is the perovskite SrTiO\textsubscript{3} (STO),\textsuperscript{8-10} as illustrated in Fig.1 for its crystalline and electronic structures\textsuperscript{11-13}. However, mechanisms underlying the enhancement of the ionic conductivity and the ORR activity remain topics which are hotly debated\textsuperscript{14}. Moreover, the atomic-scale design and synthesis principles of complex oxide heterostructures developed exclusively in the electronic community have rarely been applied to the research of ionic conductors and electrocatalysts. In particular, a bridge between the atomically engineered electronic oxide interfaces and the ionic oxide interfaces remains missing. Herein, we summarized the recent progress in the creation and characterization of advanced materials of conducting oxide interfaces for electronics. The
perspectives on applying conducting oxide interfaces for quantum devices and on using the
design principles to create future electrocatalysts are also addressed. Note that the two
techniques widely used to grow crystalline complex oxide films are: (i) pulsed laser
deposition (PLD) and (ii) molecular beam epitaxy (MBE). For their physical mechanisms and
the film growth dynamics, the readers can refer to a former review written by Chambers.¹⁵

2. Fundamental physics and chemistry of conducting oxide interfaces

One of the central issues concerning the engineered oxide interfaces is to understand and
control the interface interactions which consist of two fundamental aspects: (i) interfacial
charge reconstructions—electronic charge transfer; and (ii) interfacial atom transport—
intermixing and/or chemical reactions.

2.1 Band alignment and charge transfer at oxide interfaces

At the heterointerface between two semiconductors or oxides, the mismatch of the work
functions will result in electronic charge being transferred between the two materials, i.e.
charge transfer occurs across the heterointerface to equalize the chemical potential (i.e. Fermi
level) on both sides. The understanding of the mechanism underlying charge transfer is of the
utmost importance, as it determines the origin of the charge carriers and sets the design rules
for the growth sequence as well as band alignment. While the energy band alignment of
conventional semiconductors is quite well understood¹⁶, systematic experimental studies on
oxides are still missing. During the past several years, extensive experimentation has been
performed to determine the intrinsic band-alignment of most functional oxides (Fig. 2)¹⁷ as
well as those of 3d and 5d complex oxide heterostructures. This band alignment offers a
rationale for the estimation of valence band offsets at intimate contacts between different
materials. Notably, the charge transfer at complex oxide interfaces is generally much more
complex than those of conventional semiconductors, as the energy bands in correlated oxides
are dynamic, i.e. they respond dramatically to changes in doping, strain, and the
accompanying changes in long range magnetic and orbital ordering.¹⁸

Generally, the energy band alignment at contacts of different materials can be determined by
X-ray photoelectron spectroscopy. For insulating oxides, such as SrTiO₃, the band-alignment
and/or charge transfer with another complex oxide can be determined alternatively by making
epitaxial Schottky or p-n junctions consisting of Nb-doped SrTiO₃ (Nb:STO) and the target
oxides.¹⁹,²⁰ Assuming that the work function is almost the same as the electron affinity in the
Nb:STO, the work function of the target oxides can be estimated as the sum of the electron affinity of STO and the difference of the Fermi levels between the oxide and Nb:STO, determined by the Schottky barrier height and built-in potential of the junction. Figure 3 shows the relative energy band alignment between STO and the other two typical complex oxides, manganites (La\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3}) and cuprates.\textsuperscript{18} As we can see, the Fermi level of most manganites and cuprates is lower than that of the Nb-doped STO. This nontrivial information indicates that most transitional metal oxides could be used as an electron sink when placed in proximity to the surface or interface STO 2DEGs as discussed later.\textsuperscript{21,22}

Another remarkable property of charge transfer at oxide interface is its short-range transfer length on the order of 1-4 nm,\textsuperscript{23} and due to the strong electron correlation, a large number of charge carriers in perovskite oxides tend to localize on a specific site and exhibit normally a heavy effective mass. This implies a rather short electron wavelength as well as a small Thomas-Fermi screening length on the order of only a few nanometers.\textsuperscript{24} As a consequence, for desired properties, it is essential to master the growth of epitaxial oxide heterostructures at the atomic level.

### 2.2 Chemical redox reactions

Besides the physical mechanisms, there is plenty of experimental evidence showing that chemical reactions play an important role in the formation of conducting oxide interfaces.\textsuperscript{25-27} The chemical interactions involve mass transport over a relatively long lattice distance. The driving force behind the mass transport in the solids is a gradient in the electrochemical potential, consisting of a gradient in the electrical potential and/or chemical potential. The chemical interaction can be generally classified into four different groups: (i) redox reaction; (ii) alloy formation; (iii) encapsulation, and (iv) interdiffusion.\textsuperscript{28} Chemical redox reactions and cation interdiffusion have often been suggested as the origin of interface conduction at the polar LaAlO\textsubscript{3}/STO interfaces,\textsuperscript{25,27} though this view is hotly debated. Here we focus mainly on the redox reaction on the STO substrate by oxidizing the oxide overlayer and reducing the STO surface\textsuperscript{29}. The chemical redox reactions depend strongly on the substrate temperature and oxygen background pressure during film growth. Therefore, they often show thermodynamic and kinetic limits as well as extreme sensitivity to to electrochemical reaction conditions, rendering them difficult to investigate by conventional surface-science techniques. Moreover, nonequilibrium thermodynamics and reaction kinetics must be also considered. Consequently, similar conducting oxide interfaces may show dramatically different behavior under thermodynamic equilibrium heating procedures\textsuperscript{30}.
3 The conducting surface and interfaces of SrTiO$_3$ for electronics

As silicon is the basis of modern microelectronics, the perovskite oxide insulator, STO, is the foundation of the emerging field of oxide electronics, as it shows reasonably good lattice-match with most of other functional oxides with perovskite, spinel or fluorite crystalline structures. This facilitates the possibility to combining various functional oxides into a single epitaxial heterostructure$^{21-33}$. Moreover, unlike the conducting states of conventional semiconductor heterostructures, which are derived from $sp$ hybrid orbitals having a largely covalent nature, the conduction in STO originates from strongly correlated Ti $3d$-electrons as illustrated in Fig.1, where the orbitals have a strong coupling with the lattice, charge and spin degrees of freedom. The strong electronic correlations give rise to a variety of emergent physical properties.$^{34}$ Therefore, since the discovery of the 2DEG at LAO/STO interface in 2004,$^8$ significant attention has been focused on the exploration of exotic and unusual electronic properties, such as ferromagnetism$^{35-37}$, superconductivity$^{38-40}$, quantum Hall effect$^{41-43}$, tunable spin-orbit coupling$^{44-46}$ and sensitivity to external light illumination$^{47}$. Additionally, the search for alternative systems with better properties has resulted in the discovery of a number of new material systems of conducting oxide interfaces and surfaces. In the following, the representative 2DEG systems based on STO and the primary mechanisms underlying the surface/interface conduction are summarized.

3.1 2DEGs at polar/non-polar oxide interfaces

In the study of the metallic conduction created at the interface of LAO/STO heterostructures, much effort is directed at revealing the origin of the interface conduction. In simple ionic terms, LAO is composed of charged layers of ($\text{La}^{3+}\text{O}_2^-$)$^+$ and ($\text{Al}^{3+}\text{O}_2^-$)$^-$, whereas the terminated planes of STO, ($\text{Ti}^{4+}\text{O}_2^-$)$^0$ and ($\text{Sr}^{2+}\text{O}_2^-$)$^0$, are formally neutral, as shown in Fig.4. If the interface is abrupt, the polar discontinuity between ($\text{La}^{3+}\text{O}_2^-$)$^+$/($\text{Ti}^{4+}\text{O}_2^-$)$^0$ or ($\text{Al}^{3+}\text{O}_2^-$)$^-$/($\text{Sr}^{2+}\text{O}_2^-$)$^0$ will create a built-in potential in the LAO film. The accumulation of this potential to a large enough value, which is comparable to the band-gap of STO, 3.2 eV, will result in an injection of carriers from the film surface into the interface, thus forming a 2DEG$^{48}$ (Fig.4b). However, as a matter of fact, the hallmark of this microscopic view of a pure electronic reconstruction scenario—the huge potential drop across the LAO over-layer—has experimentally remained elusive so far. Alternatively, recent measurements performed by soft x-ray angle-resolved resonant photoelectron spectroscopy$^{49}$, as well as theoretical calculations of electronic and defect properties of LAO/STO interfaces by first principles$^{50,51}$, reveal a
promising modified electronic reconstruction scenario: the built-in potential in the LAO is compensated by positively charged surface defects such as O vacancies or other in-gap states on the LAO side, which act as charge donors (Fig.4c). Notably, since there are also extensive redox reactions on the STO surface when exposure to oxygen-deficient LAO films, for a long time, it has been extremely challenging to isolate the sought-after pure electronic reconstruction effect from the extrinsic doping effects induced by formation of oxygen vacancies. As discussed in section 3.6, this could be achieved by selecting a suitable buffer layer at the interface of LAO/STO.

The conduction of the LAO/STO interface is extremely sensitive to the film growth temperature and oxygen background pressure. Generally, when the LAO film is grown at a temperature above 700 °C and at low oxygen pressure less than about 10⁻⁶ mbar, the conduction detected is three dimensional and is dominated by oxygen defects, which extends deeply into or through the whole substrate. It is generally accepted that for samples grown at higher pressure (over about 10⁻⁵ mbar) the conduction is confined to the interface. Additionally, with the purpose to suppress the formation of oxygen vacancies, most samples are subject to post annealing at high oxygen pressure, which might have a deleterious effect on the carrier mobility. Carrier mobility is one of the most sensitive measures of the purity and cleanliness of a material. The typical 2D electron mobility in LAO/STO polar interfaces is ~10 cm²V⁻¹s⁻¹ at room temperature, and ~1000 cm²V⁻¹s⁻¹ at 2 K (Figure 5a), with a sheet carrier density, nₛ, in the range of 10¹³-10¹⁴ cm⁻². This mobility is still much lower than those for 3D oxygen-deficient STO single crystals and La-doped STO epitaxial films, amounting to 1.3×10⁴ cm²V⁻¹s⁻¹ and 3.2×10⁴ cm²V⁻¹s⁻¹ at 2 K, respectively. Although the electron mobility remains below 10 cm²V⁻¹s⁻¹ at room temperature, there have been reports that the mobility of STO 2DEGs at low temperatures can be increased to comparable or 4-6 times higher than that of the bulk mobility by surface or interface engineering.

Although the mechanism underlying the mobility enhancement induced by surface engineering remains unclear, the mobility enhancement induced by the interface engineering with a buffered layer could result from a modulation doping effect, as discussed in Section 3.5. Notably, in comparison with the conventional semiconductor heterostructures, such as GaAs, where the carrier mobility has been increased continuously over the past 40 years (Fig.5b), the mobility enhancement in the oxide 2DEGs is just starting.

3.2 Surface/interfacial 2DEGs due to chemical doping or interface redox reactions
Besides the intensively investigated 2DEG induced by the interface polar discontinuity, the most conventional way to create STO 2DEG is the trilayer homostructure of La or Nb-doped STO sandwiched between two undoped STO, which can show reasonably high mobility when the doping level is low\textsuperscript{43}. Moreover, the recently discovered 2DEGs at the surface of fractured STO under exposure of the surface to intense ultraviolet light\textsuperscript{60-63}, and at the interface between STO and an insulating amorphous overlayer\textsuperscript{29}, also show similar and nontrival low temperature physical properties. A notable feature of these three systems is the presence of localized carriers trapped in the in-gap states, as illustrated in Fig.6. As a consequence, when the carrier density is high (normally above the order of $10^{13}$ cm$^{-2}$), the temperature dependent carrier density often shows carrier freezing out phenomena\textsuperscript{64}.

The 2DEG in amorphous STO heterostructures (Fig.6c) results from interfacial redox reaction and is of particular interest because the interface conduction can be enhanced or suppressed by selecting different capping layers. For the ABO$_3$ perovskite-type interface of intensive research, where A is an electropositive cation such as an alkali, alkaline-earth or rare-earth ion, the chemical reaction and electron transfer across the perovskite-type interface is expected to depend primarily on the electronegativity and coordination environment of the transition metal ions on the $B$ site. Taking this into account, the perovskite oxide interface investigated so far can be divided into three families: (1) the metallic interfaces of crystalline LAO/STO\textsuperscript{8}, crystalline LaTiO$_3$/STO\textsuperscript{65}, crystalline CaZrO$_3$/STO\textsuperscript{66}, amorphous LAO/STO\textsuperscript{29}, amorphous STO/STO\textsuperscript{29}, amorphous YSZ/STO\textsuperscript{29}, and amorphous CaHfO$_3$/STO\textsuperscript{67}, which fulfill all criteria for oxide-oxide interface redox reactions of $\Delta H_f^O$<-350 kJ/(mol O) and 3.75 eV<$\varphi$<-4.4 eV, where $\Delta H_f^O$ and $\varphi$ is the formation heat of metal oxide and the work function of the $B$-site metal, respectively, as illustrated in Fig.7b; (2) the insulating interfaces of LaFeO$_3$/STO\textsuperscript{68} and LaMnO$_3$/STO\textsuperscript{69} which have $\Delta H_f^O$>-350 kJ/(mol O) and $\varphi$>4.0 eV; and (3) the either metallic interfaces of crystalline LaVO$_3$/STO\textsuperscript{70} and crystalline LaGaO$_3$/STO\textsuperscript{71} or the insulating interface of LaCrO$_3$/STO\textsuperscript{72}, where the $B$-site metals reside in an intermediate region of -350 kJ/(mol O) <$\Delta H_f^O$<-450 kJ/(mol O) and 4.1 eV<$\varphi$<4.5 eV. Therefore, the appearance or the lack of interface redox reaction provides an inspiring clue on the metallic and insulating nature of oxide interfaces reported so far. Note that for the manganite/titanate heterointerface, since the lowest unoccupied state in STO (Ti t$_{2g}$) is about 1eV higher than that of the manganite film (Mn e$_g$), the pure electronic reconstruction mechanism can also explain the insulating behavior as charge transfer or reconstruction occurs predominantly in the MnO$_2$ sublayers in proximity to the interface\textsuperscript{64,69}. 


The redox-reaction mechanism, which occurs even at room temperature, can also explain the other forms of conducting STO-based and TiO$_2$-based oxide interfaces when Al- or Ti containing oxides are involved during the fabrication by pulsed laser deposition, atomic layer deposition, electron beam evaporation and even chemical spin coating. Furthermore, it provides an additional approach to tune the interface conduction by controlling the interfacial redox reaction during deposition. For example, by improving the chemical reactivity of the plasma plume through deposition the LAO film in argon rather than in oxygen, the amorphous LAO/STO conduction can be enhanced. Moreover, the conductivity of amorphous-LAO/STO interfaces is also found to be modified by an external electric field provided \textit{in-situ} through a biased, truncated cone electrode (-10 V ≤ $V_{\text{bias}}$ ≤ 20 V) during film deposition. By modulating the charge balance of the plasma plume, a substantial surface charge is found to transiently build up during the initial phase of the film growth when the truncated cone electrode is biased. The presence of this huge surface potential is expected to greatly influence the surface/plasma interaction during film deposition. More specifically, experimental observations seem consistent with a lowering of the incoming Al-ion flux by the applied bias, which shifts the interfacial conduction of $d$-LAO/STO from metallic over semiconducting to insulating transport mode. This remarkable behaviour further indicates the importance of Al-ion flux on the amount of near-interface oxygen vacancies formed at the STO surface and therefore the interface conduction, which is also tunable by external electric field.

### 3.3 2DEGs at non-polar oxide interfaces induced by strain-induced polarization

Besides interfacial polar discontinuity, spontaneous and/or piezoelectric polarizations have been found to result in high-mobility 2DEGs in both traditional semiconductor materials such as III-V semiconductor AlGaN/GaN compound heterostructures and the binary oxide heterostructures of ZnMgO/ZnO. Recently, strain induced polarization has also been found to result in a high mobility 2DEG in STO heterostructures at an otherwise nonpolar perovskite-type interface of (001) CaZrO$_3$/STO (CZO/STO). In these systems, the 2DEG carriers normally originate from the ionized surface donor state. The spontaneous and/or piezoelectric polarization in the top film provides the driving force to collect the electrons in the quantum well. Notably, as illustrated in Fig.8, the CZO/STO heterostructure shows both atomically sharp interfaces and extremely high electron mobility exceeding 60000 cm$^2$V$^{-1}$s$^{-1}$ at 2 K, which is nearly independent of the film thickness. There is also a critical thickness of $t_c=6$ uc for the presence of interface conduction (Fig.8c). This is consistent with the model based on the polarization induced charge transfer, for ultrathin CZO films with a...
thickness below $t_c$, the ionized donor surface states, which are sufficiently deep and below the conduction band of CZO with an energy $E_D$, lie far below the conduction band of STO (Fig. 8d). In this case, no 2DEG is formed. Increasing the CZO film thickness normally lifts the energy of the surface donor states. At the critical thickness, the surface donor energy reaches the bottom of the conduction band of STO, as demonstrated in Fig. 8e. Electrons, at the same time, are transferred to the empty conduction band of STO at the interface, creating the 2DEG. Until all the surface states are empty, in the ideal case, the Fermi level remains at the donor energy while more and more electrons are transferred with increasing the film thickness. Note that first-principles electronic structure calculations predict that the polarization direction and $t_c$ of the CZO could depend on the surface termination of CZO film.\[^{84}\] More recently, using conductive atomic force microscopy lithography, extremely narrow nanowires between 1.2 nm to 2.8 nm and various quantum devices were realized at the CZO/STO interface. Notably, the widths of the nanowires remain narrow at most writing voltages\[^{85}\], in contrast to nanowires formed at the LAO/STO interface, where the wire width depends sensitively on the writing voltage\[^{86}\]. Therefore, much more exotic properties and functionality are awaiting to be explored for the sharp and high mobility CZO/STO interface.

### 3.4 Modulation-doped complex oxide interfaces

Most 2DEGs in STO heterostructures show a high carrier density above $10^{13}$ cm$^{-2}$. These electrons ($t_{2g}$ electrons) come generally in two species\[^{11}\], $d_{xy}$ and $d_{xz}/d_{yz}$ (where $z$ is perpendicular to the 2D layers), as illustrated in Fig.1. The $d_{xy}$ component accounts for the majority of the 2DEG charge. The $d_{xy}$ electrons reside at or in the immediate proximity of the interface, but exhibit a rather low mobility. In contrast, $d_{xz}$ or $d_{yz}$ electrons extend further away from the interface and amount to only a small fraction of the 2DEG population. Yet, their mobilities reach much higher values than that of the $d_{xy}$ states\[^{11}\]. This intrinsic electronic structure (the coexistence of both high and low mobility carriers on the same side of the interface) prevents the application of the conventional modulation-doping technique to enhance the electron mobility where a spacer layer is introduced which separates spatially the electron gas from its charged donors on the sample surface\[^{87,88}\]. Recently, by inserting a buffer layer of LaMnO$_3$ (LMO)-based manganite as thin as one single unit cell (uc), e.g. La$_{1-x}$Sr$_x$MnO$_3$ (LSMO, $x$=0, 1/8, and 1/3), at the interface as shown in Fig.9a, a charge-transfer-induced modulation doping is achieved for the 2DEG in amorphous LAO/STO with a huge mobility enhancement of more than two orders of magnitude in addition to a remarkable decrease in the carrier density (Fig.9 b and c).\[^{21,22}\] In contrast to the spacer layer used in
conventional semiconductors as illustrated in Fig. 9d, the LMO-based spacer at oxide interfaces can act as an additional electron sink because it has an empty or partially filled subband lower than the conduction bands of STO (Fig. 9e and also Fig. 3). Furthermore, in-depth X-ray reflectivity and oxygen isotope tracing measurements reveal that the manganite can also suppress strongly the formation of oxygen vacancies on the STO side. It is further revealed that the carriers of the interface 2DEGs show negligible dependence on the Sr-doping level of the spacer. In contrast, a large tunability of the interface conduction was achieved recently by doping LaMnO$_3$ into the LAO top layers, i.e. via the formation of a diluted oxide interface as demonstrated in Fig. 10. By increasing the Mn-doping level of LaAl$_{1-x}$Mn$_x$O$_3$(LAMO)/STO ($0 \leq x \leq 1$), the interface undergoes a Lifshitz transition at a critical carrier density of $n_c = 2.8 \times 10^{13}$ cm$^{-2}$, where a peak $T_{SC} \approx 255$ mK of the superconducting transition temperature is observed. Moreover, at $x = 0.3$, where the metallic interface is populated by only $d_{xy}$ electrons and the LAMO becomes ferromagnetic, a possible coexistence of superconductivity and ferromagnetism is achieved. This provides a unique and effective way to tailor oxide interfaces for designing on-demand electronic and spintronic devices.

3.5 Magnetic 2DEGs at STO-based heterointerfaces

The possibility to obtain a spin-polarized 2DEG based on STO 2DEGs provides also new opportunities for spintronics. Although there are reports on the possible magnetic ordering in LAO/STO heterostructures, these samples tend to be insulating or show signatures related to the interaction between itinerant electrons and localized magnetic moments. To introduce strong/unambiguous magnetism into the highly conductive LAO/STO, three ways have turned out to be effective so far. The first is the magnetic proximity effect induced by a EuTiO$_3$-ferromagnetic buffer layer at the LAO/STO interface. The spin polarization emerges below the ferromagnetic transition temperature of the EuTiO$_3$ epitaxial layer ($T=6–8$ K) and is due to the exchange interaction between the magnetic moments of Eu-$4f$ and of Ti-$3d$ electrons as confirmed by X-ray magnetic circular dichroism (XMCD) measurements. A second effective way is the introduction of the ferromagnetism into the top layer of LAO or the introduction of a ferromagnetic capping layer (mostly metal) directly on STO as demonstrated in the cases of the magnetic diluted oxide interface of LAMO/STO as well as EuO/STO, and $M$Al$_2$O$_4$ ($M=$Ni, Co)/STO. Notably, both the LAO/EuTiO$_3$/STO and LAMO/STO systems show signatures of the coexistence of ferromagnetism and superconductivity, although their carriers come from two-band and single band conduction.
respectively. The final and the direct approach towards magnetic 2DEGs is the conventional doping with magnetic ions.\textsuperscript{94-96} For example, a robust anomalous Hall effect\textsuperscript{95} and large negative magnetoresistance\textsuperscript{96} were observed when Fe-doped STO (Fe-STO) was used as the substrate for the fabrication of the conducting interface of LAO/Fe-STO. The anomalous Hall effect has been observed up to room temperature.\textsuperscript{95} On the other hand, since the magnetic Fe dopant is localized within the STO substrate, the mobility of this type of 2DEG is generally very low (below 100 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} at low temperatures).

4. Atomic and elemental characterization of conducting oxide interfaces

To understand the origin and detailed nature of conducting interfaces in correlated oxides, many experimental probes are often employed, particularly high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) imaging with electron energy loss spectroscopy (EELS) and energy dispersive X-ray (EDX) spectroscopy measurements.\textsuperscript{6,97} To study buried interfaces in a non-destructive manner, a particularly useful technique is that of X-ray spectroscopy.\textsuperscript{7} In particular, for interfaces where 3\textit{d} transition metals are active elements (e.g. for STO-based interfaces), X-ray absorption spectroscopy (XAS) is often used to probe the L\textsubscript{2,3} core level resonances of the transition metal element. The resulting spectra carry detailed information about the local electronic and magnetic structure of the element under study.\textsuperscript{98} Figure 11 shows the sensitivity of Ti L\textsubscript{2,3} scattering factors to the valence state of Ti, and thus the presence or absence of a 2DEG. As shown in the figure, XAS can be made more surface- or bulk-sensitive via the detection method used (electron yield or fluorescence yield, respectively).

Salluzzo et al. used XAS to reveal orbital reconstruction at the (001) LaAlO\textsubscript{3}/SrTiO\textsubscript{3} interface\textsuperscript{99}, where a tetragonal symmetry breaking lifts the degeneracy of the \textit{t}\textsubscript{2g} Ti 3\textit{d} orbitals, shifting the \textit{d}\textsubscript{xy} orbital lower in energy compared to the \textit{d}\textsubscript{zx} and \textit{d}\textsubscript{yz} near the interface. This lowering of the \textit{d}\textsubscript{xy} orbital energy indicates that it will be preferentially occupied by the 2DEG near the interface, and will thus determine the 2DEG transport properties. Later XAS studies
revealed orbital polarization with a different symmetry at (110) LAO/STO interfaces\textsuperscript{100}, as well as magnetism at oxygen deficient (001) LAO/STO interfaces\textsuperscript{101}.

As shown in Figure 11, X-ray absorption is a technique which averages over the probing depth studied (either a few nm or several tens of nm, depending on the type of detection), but a strongly enhanced interface sensitivity can be achieved with the technique of resonant x-ray reflectometry (RXR)\textsuperscript{7}. With RXR, one probes the same fundamental scattering tensors as in XAS, but via the specular reflection rather than absorption of X-rays, allowing for naturally quantitative measurement and analysis having inherent interface sensitivity offered by the reflection process. RXR is sensitive to elemental concentrations as well as detailed local electronic and magnetic structures with sub-angstrom depth resolution. Macke \textit{et al.} demonstrated the high sensitivity of RXR, by detecting a single monolayer of La\textsubscript{0.005}Sr\textsubscript{0.995}TiO\textsubscript{3} buried within a homoepitaxially grown STO film on a STO substrate\textsuperscript{7}.

Using RXR, the authors characterized the concentration of the La dopant as well as the interdiffusion of La into adjacent monolayers, highlighting the strong elemental sensitivity. Later, RXR was demonstrated to be valence sensitive, where polarity driven electronic reconstruction was detected at a polar surface of a LaCoO\textsubscript{3} film\textsuperscript{102}. The authors observed a valence change of the Co atoms near the polar surface, in accordance with a polarity driven electronic reconstruction. Additionally, an RXR study detected orbital polarizations near buried interfaces in a LaNiO\textsubscript{3} heterostructure\textsuperscript{103} while investigating the possibility of engineering a cuprate-like Fermi surface in a nickelate material. Finally, it was shown that RXR can be used to determine substrate terminations with atomic plane resolution\textsuperscript{104}.

When applied particularly to conducting STO-based interfaces, the relatively new technique of RXR has already provided important insights.\textsuperscript{21,64} A reduction in 2DEG density was detected via RXR in high-mobility modulation-doped amorphous LAO/STO interfaces\textsuperscript{21}. This finding provided important insight to reveal the mechanism behind the buffer layer induced high mobility 2DEG, which was discussed previously in section 3.3. Besides electronic
reconstruction, the RXR techniques also provides valuable information on the interfacial redox reactions. Figure 12 provides an overview of the application of RXR to study manganite buffered interfaces between disordered yttria-stabilized zirconia (d-YSZ) and STO, which show clear competition between pure electronic reconstruction and interfacial redox reactions. Panel (a) depicts schematically (top) and quantitatively (bottom) the elemental and valence concentrations extracted from RXR analysis of a conducting d-YSZ/STO heterostructure. A large fraction of Ti$^{3+}$ is detected in the STO near the interface, and a corresponding dip in the oxygen density is present in this region, providing evidence for carriers supplied by redox-induced oxygen vacancies. Panel (b) shows results for an epitaxial, insulating LSMO buffer layer on STO, where electronic reconstruction yields Mn$^{2+}$ at the interface. Some Mn$^{2+}$ is also observed at the surface due to slight degradation, common in LSMO films. Finally, panel (c) shows results for a complete d-YSZ/LSMO/STO heterostructure. The RXR analysis reveals polarity induced electronic reconstruction to Mn$^{2+}$ at the lower interface, and redox induced Mn$^{2+}$ at the upper interface. At the upper interface, distinct Mn sites having octahedral and tetrahedral symmetry are observed, indicative of the brownmillerite structure in the LSMO present due to oxygen vacancies. The interpretation of the results is that the uneven potential due to the brownmillerite layer causes some charge transfer from the Mn$^{2+}$ at the lower interface into the STO, yielding the exceptionally high mobility 2DEG. Panels (d) and (e) provide some representative RXR spectra and fits, with complete data sets available in Ref.64.

The analysis of RXR data is generally rather complex, but important recent advances have been made. Macke et al. have developed the ReMagX program, which is now widely used for modelling of the RXR process. Additionally, the program QUAD can be used to efficiently simulate both resonant diffraction and reflection within the same model with full dynamic effects, allowing for example the simultaneous modelling of reflectivity and magnetic
scattering in heterostructures\textsuperscript{108}. An additional recent development is a theory-restricted modelling of the RXR signal during analysis\textsuperscript{109}. It is noteworthy that resonant X-ray reflectometry is a complementary technique to STEM-EELS\textsuperscript{97}, which also provides access to spatially resolved atomic scattering tensors at core level resonance energies. Both techniques have distinct advantages: RXR is non-destructive, has a strong signal, straight-forward polarization dependence, and flexible sample environment, whereas STEM-EELS has the advantage of operating directly in real space and also providing lateral information (i.e. in the direction parallel to interfaces). The combination of both techniques can yield a very comprehensive view of interface properties, as demonstrated in recent studies.\textsuperscript{21}

5. Concluding remarks and outlook
The materials systems for the 3\textit{d} oxide 2DEGs have gone much beyond the LAO/STO polar interfaces and we have also learned various ways to improve the quality of the interface conduction by controlling the electronic and/or chemical interactions, taking into account the insights provided by the advanced characterization techniques. The samples with extreme cleanness are of particular interest as they provide unforeseen opportunities to discover new quantum phenomena at low temperatures. Moreover, the engineered charge transfer and redox reactions at oxide interfaces are not only important for electronics but also for the search of electrocatalysts of mixed electronic and ionic oxide interfaces. The rich landscape of quantum transport phenomena in STO-based nanostructures\textsuperscript{110,111} and field-effect transistors (FETs) as building blocks of integrated circuits of complex oxides\textsuperscript{112,113} have been demonstrated, and unprecedented discoveries are expected in the following two research areas:

(a) **Quantum transport and quantum devices based on STO 2DEGs.**
When the charge carriers are confined to a two-dimensional system, the Hall resistance can become exactly quantized under external magnetic field, i.e. the quantum Hall effect can be observed. Such research performed on the modulation-doped amorphous LAO/STO interface with extremely high electron mobility and low carrier density reveals that the single interface consists of multiple quantum wells.\textsuperscript{41} This could be due to the strong electron correlations that constrain a number of electrons at a given lattice site, particularly the TiO\textsubscript{6} octahedra, intrinsic to STO interfaces.\textsuperscript{114} Importantly, when this unique property is coupled to the large Rashba
spin-orbit interaction, what will be the characteristic features of quantum devices based on complex oxide interface? Moreover, as the conducting oxide interface turns ferromagnetic which leads to anomalous Hall effects in the normal state, what will be the quantized version of this anomalous Hall effect? Besides the above quantum phenomena, quantum coherent devices, such as tunneling junctions or superconducting qubits, important in magnetic sensors as well as information processing technology, can also be designed.

(b) Atomically engineered oxide interfaces for electrocatalysts

At relatively high temperatures, most perovskite oxides also show mixed electronic and ionic conductivity, important for oxygen redox reactions. The conventional way to tune the intrinsic activity of perovskite oxides is by chemical doping, which often introduces unintentional impurities. Without introducing unintentional defects, interfacial electronic reconstruction and redox reactions can also be used to tune these chemical activities. Notably, the recent development of sophisticated tools for growing complex oxides as thin films with atomic-layer sensitivity and control has rarely been applied to the search for new oxide electrocatalysts.

In this work, we have summarized the recent progress in the material science of conducting oxide interfaces for electronics. The physical and chemical mechanisms and the technical progress of these atomically engineered oxide interfaces could provide an intriguing opportunity for the conception and design of mixed electronic and ionic conducting oxide interfaces that go beyond the limits of state-of-the-art perovskite electrocatalysts.

Acknowledgements

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[106] Macke et al., http://quad.x-ray.center


Figure 1. The perovskite structure of SrTiO$_3$ (a) and the electronic structure of SrTiO$_3$-based 2DEGs (c). The 2DEG electrons ($t_{2g}$ electrons) come in two species, $d_{xy}$ and $d_{xz}/d_{yz}$ (as demonstrated in b, $z$ is perpendicular to the 2D layers) with different spatial dispersion. The $d_{xy}$ electrons dominate the carrier population but exhibit a relatively lower carrier mobility. Reproduced with permission from ref. [11-13]. Copyright 2013, Nature Publishing Group and American Physical Society.
Figure 2 Energy band alignment at contacts of different oxides determined from a large set of interface experiments with photoelectron spectroscopy. The valence band maximum energy of SnO$_2$ is represented by the dashed line and is set as a reference of the energy scale as a guide to the eye. Vertical numbers refer to the band gaps of the materials in eV. Horizontal numbers refer to the offset of the valence band maximum for each material with respect to the valence band maximum of SnO$_2$ in eV. The valence band discontinuity between any combinations can be obtained assuming transitivity by subtracting the respective offsets to SnO$_2$.

Fig. 3 Energy band alignment between two typical complex oxides, manganites (La$_{1-x}$Sr$_x$MnO$_3$) and cuprates (LCO: La$_2$CuO$_4$, NCO: Nd$_2$CuO$_4$, SCO: Sm$_2$CuO$_4$, and YBCO: YBa$_2$Cu$_3$O$_{y}$) with respect to Nb-doped SrTiO$_3$ (Nb:STO). Reproduced with permission from ref. [18]. Copyright 2007, American Physical Society.
Fig. 4 (a) The pure electronic polar catastrophe scenario: a building-up of electric potential upon increasing the layers of polar LAO is essential. (b) Schematic band diagram for the standard electronic reconstruction scenario in LAO/STO. Electronic reconstruction occurs when the valence band maximum is lifted to the level of the conduction band bottom of STO. (c) Tentative band situation with the inclusion of O vacancies at the LAO surface or other in-gap states as the charge donors for electronic reconstruction.

Fig. 5 Landmark electron mobilities in the history of (a) complex oxide 2DEGs based on LAO/STO in comparison with that of (b) GaAs. Reproduced with permission from ref. [59]. Copyright 2003, Elsevier. The mobility of 2DEG at the interface of crystalline LAO/STO shows a limit around 5,000 cm$^2$V$^{-1}$s$^{-1}$, which is lower than the bulk value (approximately 20,000 cm$^2$V$^{-1}$s$^{-1}$ at 2 K$^{55}$). But the spinel/perovskite interface of $\gamma$-Al$_2$O$_3$/STO$^{10}$, nonpolar oxide interface CaZrO$_3$/STO$^{66}$ and buffered $d$-LAO/STO$^{21}$ all show electron mobility higher than that of the bulk.
Figure 6. Schematic picture of device structure (a-c) and electronic band structure (d-f) of surface 2DEG, homointerfacial 2DEG, and the heterointerfacial 2DEG, respectively, based on STO.

Fig. 7 (a) Sketch of redox reaction at oxide interfaces; reproduced with permission from ref. [29]. Copyright 2011, American Chemical Society. (b) Formation heat of metal oxides versus the work function of B-site metals for the ABO$_3$/STO (A=La) perovskite-type interface. For metallic interfaces, the B site metals locate mainly in the region of $\Delta H_f^{\text{O}} < 350$ kJ/(mol O) and $3.75 \text{ eV} < \phi < 4.4 \text{ eV}$ (Square and Diamond). The dot line indicates the border of the redox reaction for metals on the STO surface$^{28}$.

((For Essays, Feature Articles, Progress Reports, and Reviews, please insert up to three author biographies and photographs here, max. 100 words each))

Author Photograph(s) ((40 mm broad, 50 mm high, gray scale))
The table of contents entry should be 50–60 words long and should be written in the present tense and impersonal style (i.e., avoid we). The text should be different from the abstract text.

**Fig.8** High mobility 2DEG at the nominally nonpolar CZO/STO interface. (a) A typical HAADF-STEM image across the heterointerface. (b) Temperature dependence of the interface sheet resistance, $R_s$, at different CZO film thickness (c) sheet carrier density as a function of the film thickness, (d) and (e) Sketch of the band alignment before and after the formation of 2DEG, respectively, at the CZO/STO heterointerface. Reproduced with permission from ref. [66]. Copyright 2015, American Chemical Society.
Modulation doping of STO-based heterostructures. (a) TEM structure of a LSMO-buffered \(d\)-LAO/STO interface; (b) and (c), The temperature dependence of carrier density, \(n_s\), and mobility, \(\mu\), respectively for the buffered and unbuffered \(d\)-LAO/STO interfaces. The unbuffered sample always shows a carrier freeze-out at around 100 K, while, the buffered samples exhibit remarkable temperature independent \(n_s\) and a large \(\mu\) often exceeding approximately 10000 cm\(^2\)V\(^{-1}\)s\(^{-1}\) at 2 K. Reproduced with permission from ref. [21]. Copyright 2015, Nature Publishing Group. (d) and (e) The principle of modulation-doping at semiconductor and complex oxide interfaces, respectively. In modulation-doped semiconductors, the electrons are spatially separated from their donors by a spacer, and ionized impurity scattering is thus reduced. However, in modulation-doping oxide interfaces, the spacer should be also able to trap the low mobility carriers by the presence of empty or partially filled bands below the Fermi level of STO 2DEG. \(E_C\) and \(E_V\) denote the conduction band edge and valence band edge, respectively, and \(E_F\) denotes the Fermi level.
Fig. 10. 2DEG in the diluted LAMO/STO heterostructures. (a) Sketch of the structure of Mn-dopants on the polar LAO side; (b) Temperature dependence of the sheet resistance \( R_s \) at different Mn doping concentrations; (c) Phase diagram of LAMO/STO heterostructures as a function of carrier density. At \( x = 0 \) (LAO/STO), the samples are metallic conducting with itinerant electrons occupying both \( d_{xy} \) and \( d_{z^2}/d_{yz} \) bands and becoming superconducting below 34 mK. Here, \( n_s \) denotes the total carrier density measured at 2 K. At a lower carrier density of \( n_c = 2.8 \times 10^{13} \text{ cm}^{-2} \) (\( x = 0.225 \)), the superconducting transition temperatures \( T_{SC} \) peaks at a value of 255 mK and here a Lifshitz transition point is observed. Below \( n_c \), the \( T_{SC} \) decreases and transport occurs only in the \( d_{xy} \) band until the samples turn insulating (\( n_s < 2.9 \times 10^{12} \text{ cm}^{-2} \)). For \( 2.9 \times 10^{12} \text{ cm}^{-2} \leq n_s \leq 1.1 \times 10^{13} \text{ cm}^{-2} \), the interface shows an anomalous Hall effect with occupation of only the \( d_{xy} \) band. In addition, a magnetically ordered state appears in the LAMO top film at \( T \leq 21 \text{ K} \) for \( x \geq 0.25 \), whereas no signature of magnetism is observed below this doping level. Finally, the sample in a van der Pauw geometry (\( n_s = 8.9 \times 10^{12} \text{ cm}^{-2} \)) with full superconducting transition where \( R_s = 0 \) is reached at \( T_{SC} \approx 160 \text{ mK} \) that also shows AHE is marked as filled square in the figure.

Figure 11 – X-ray spectroscopy for thin film interfaces. (a) The Ti resonant scattering factor changes strongly with the Ti valence, and can be used to probe the presence of a 2DEG in STO. XAS probes directly the imaginary component of the scattering factor \( F \). (b) Whether probed using electron yield (EY) or fluorescence yield (FY), the exponential probing depth profiles of XAS offer little interface sensitivity. RXR on the other hand involves the reflection of x-rays, which allows for significantly enhanced interface sensitivity.
Yunzhong Chen received his Ph.D. in Condensed Matter Physics in 2009 from Institute of Physics, Chinese Academy of Sciences, and the classic Doctor Technices Degree from Technical University of Denmark (DTU) in 2016. From 2009-2011, He was a post-doc at Risø National Laboratory for Sustainable Energy, Denmark and became a scientist in Department of Energy Conversion and Storage at DTU in 2011. Since 2013, he has been an associate professor at DTU Energy. His research focuses on the creation and understanding of interface phenomena in atomically engineered oxide heterostructures for high electronic and ionic conductivity, ferromagnetism, and enhanced catalytic activity.

(bio and photographs of Robert Green will be added later)

The recent progress in material science of conducting oxide interfaces based on SrTiO$_3$ is summarized. The principal mechanisms and perspectives on quantum devices and atomically engineered perovskite electrocatalysts are also discussed.

**Keyword**

Oxide interfaces, Charge transfer, Electronic reconstructions, Two-dimensional electron gases, Oxygen redox reactions
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Title: Progress and Perspectives of Atomically Engineered Perovskite Oxide Interfaces for Electronics and Electrocatalysts

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