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ABSTRACT

Oxides bring not only new properties such as superconductivity, ferro-, pyro-, and piezoelectricity, ferromagnetism, and multi-ferroicity but also ionic and catalytic properties. Such richness arises from a strong interaction between the charge, orbital, spin, and lattice degrees of freedom. Interfacing two oxide-based materials results in broken lattice symmetry as well as electronic and/or atomic reconstructions from which a wealth of new intriguing properties can emerge. Here, we provide an overview and perspective of electronic, ionic, and ionotronic properties in oxide systems with confinement designed by broken lattice symmetry.

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Transition metal oxides continue to attract paramount attention due to the large range of exciting properties they exhibit.¹ From an electronic perspective, oxides cover the range from large bandgap insulators to metals and high temperature superconductors. At high temperatures, oxides also exhibit interesting ionic properties with fast ionic transport mixed electronic and ionic conductivity and high catalytic and electrochemical properties. The properties of oxides are closely coupled to the lattice, which leads to, e.g., ferroelectricity and piezoelectricity. Breaking the lattice symmetry of bulk oxide single crystals can therefore induce prominent changes in the resulting properties. This is particularly the case when joining two or more oxides in a heterostructure where completely different electronic and ionic properties may emerge at the interface(s).

Today, modern thin film growth technologies can control the individual layers in an oxide heterostructure at the atomic level with high precision. These techniques mainly include pulsed laser deposition (PLD),² oxide molecular beam epitaxy (oxide MBE),³ and atomic layer deposition (ALD).⁴ They allow atomically engineered heterostructures and interfaces with the possibility to intentionally introduce defects by controlling the deposition parameters. Such methods are crucial for the future technology development as well as for an

analytical understanding of the interfacial phenomena. In particular, they have been used as key methods for synthesizing advanced material systems and heterostructures with highly coherent interfaces. In this paper, we provide an insight into oxide interfaces and review some of the most exciting research directions within the fields of electronics, nanoionics, and ionotronics.

The interface properties have been studied in a large number of oxide heterostructures, leading to conducting interfaces between insulators,⁵ electron mobilities exceeding $1.000.000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in ZnO,⁶ and a control of the interfacial oxygen stoichiometry, as in the case of the redox reactions in SrTiO₃.⁷ In more than a decade, heterostructures with different oxides (most noticeably LaAlO₃) deposited on SrTiO₃ have been intensely investigated. The LaAlO₃/SrTiO₃ heterostructure has since its discovery in 2004⁵ proven a fertile material system for the observation of novel physics arising from the confinement of correlated electrons at the interface. This has opened a fascinating research area resulting in many important discoveries that have been the focal point of the emerging field of multi-functional oxide nano-electronics. One of the important discoveries was that the resistance of the interface can be tuned by application of an electric field from a gate,⁸ which further led to the

discovery that numerous other physical properties were also gate-tunable.⁹⁻¹² At room temperature, the gate-induced change in the resistance was found to exceed three orders of magnitude and lead to a metal to insulator transition in proximity to a threshold film thickness for interface conduction.^{8,13} A remarkable feature is that the resistance change is quasi-stable, even when the applied electric field is turned off.^{8,13} This non-volatile resistive change could be induced on the nanoscale using a conducting atomic force microscopy tip, thereby enabling nanocircuits to be drawn at the interface for the design of on-demand devices.^{14,15} At low temperatures, a dramatic effect of electrostatic gating was also observed, leading to a complete change of the ground state where the superconducting state at the interface could be turned on and off using the gate.^{9,16} Among the plethora of fascinating phenomena of oxide interfaces,^{17,18} electron pairing in the absence of superconductivity, domain wall engineering, high electron mobility, and emergence of hole gases have recently attracted much attention and will be discussed next:

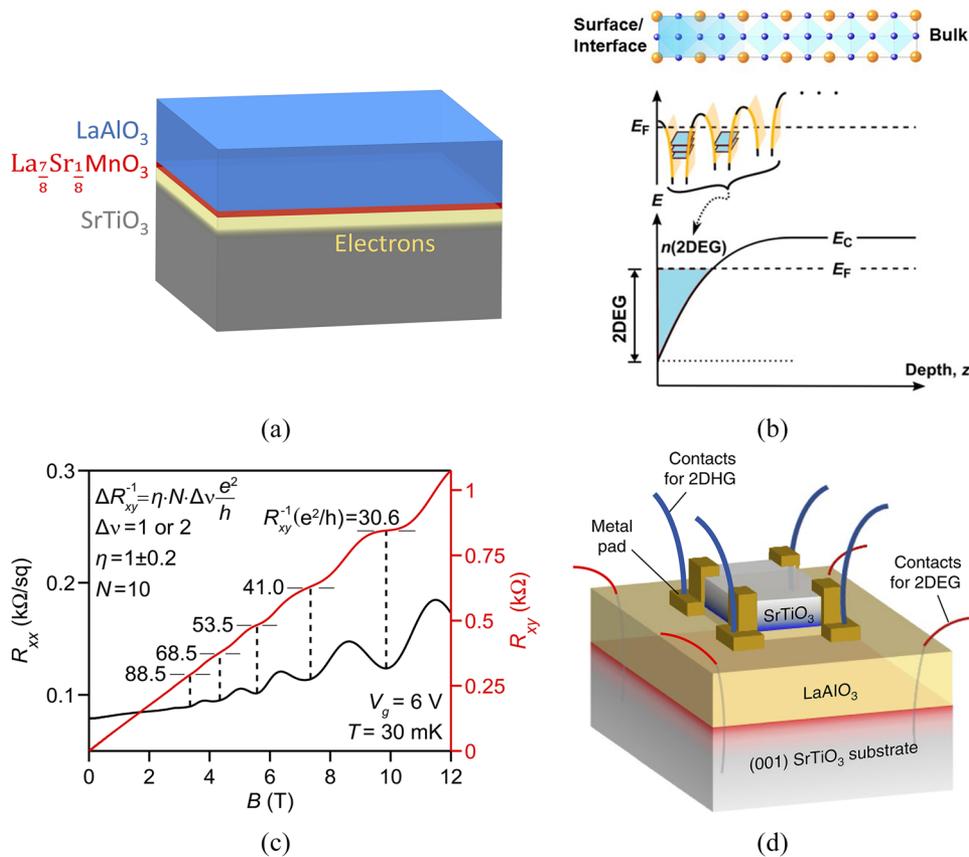
The superconducting state in the $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructure turned out to show a fascinating twist when an applied magnetic field was used to break the superconductivity. Rather than splitting the paired electrons into two normal conducting electrons, the electrons were found to remain paired even after the superconductivity was broken.¹⁹ This was realized in 2015 in a quantum dot geometry defined using a biased conducting atomic force microscopy tip (c-AFM),¹⁹ and it was later reproduced by using not only c-AFM²⁰⁻²² but also lithography.²³ The geometry allowed for determining the number of electrons added to the dot. When increasing the electron occupancy on the dot using a gate, it was found that electrons were added in pairs, even under conditions where the superconductivity was suppressed. Applying a magnetic field of the order of 1 T, much larger than that needed to break the superconductivity, resulted in breaking of the pairs. Beyond this pairing field, the electrons were added sequentially to the dot. In this way, a new material state was discovered, which today remains largely unexplored. It remains yet elusive whether the properties of this state can be useful for creating novel electronic devices. Irrespective of potential applications, the paired state provides a hitherto unseen opportunity to study the fundamental properties of a superconductor, which may in turn give hints on improving the superconducting transition temperature.

Besides the broken lattice symmetry at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface, SrTiO_3 itself also changes its lattice symmetry at low temperatures. Cooling SrTiO_3 down below 105 K induces a transition from cubic to tetragonal, resulting in domains with the tetragonal long axis oriented either along the [001], [010], or [100] crystallographic direction.^{24,25} The domain walls between the tetragonal domains turn out to exhibit properties markedly different from those observed in the interior of the domains. This is particularly the case for the domain walls in SrTiO_3 , where recent experiments suggest that the domain walls cause electron pairing,²⁰ stripy magnetic orders,²⁶ and a strain-tunable polarity.²⁷ By exploiting the small domain wall

widths as well as their writable, erasable, and movable properties, they can be used to design functional nanoelectronics. A better understanding of the domain walls as well as a delicate control of the wall location and properties is, however, required. If this is accomplished, one can for instance envision a memristive device where electric fields drive the resistance between high- and low-resistive states in a non-volatile manner using domain wall motion. Here, the low-resistive state can for instance be formed by aligning low-resistive domain walls parallel to the current flow, whereas a high-resistive state can occur by removing the domain walls or orienting them perpendicular to the current flow.^{28,29}

One of the most remarkable properties of donor-doped SrTiO_3 single crystals is their high electron mobility at low temperatures ($\sim 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).^{30,31} However, the typical electron mobility for the as-grown SrTiO_3 heterointerfaces remains more than one order lower, $\sim 1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 2 K, with a sheet carrier density in the range of 10^{13} – 10^{14} cm^{-2} .^{12,32} Fortunately, recent progress in surface and interface engineering of oxide heterostructures has enabled the realization of 2DEGs with high mobility above $10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 2 K by decreasing the carrier densities in the range of 10^{12} cm^{-2} .³³⁻³⁵ Particularly, the realization of modulation-doping of the interfacial 2DEG at disordered- $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces not only enhances the electron mobility more than 100 times but also leads to the observation of the quantum Hall effect at the LaMnO_3 (LMO) buffered $\text{LaAlO}_3/\text{SrTiO}_3$ heterointerface [see Figs. 1(a)–1(c)].³³ The latter seems to confirm the unique feature of oxide interfaces³⁶ that a single quantum well may consist of approximately 10 parallel conducting two-dimensional subbands (for a carrier density of $7.2 \times 10^{12} \text{ cm}^{-2}$).³⁷ Nevertheless, challenges remain on how the mobility of oxide interfaces can be enhanced much larger than $10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ or whether we can obtain metallic oxide interfaces with carrier densities lower than 10^{12} cm^{-2} . For conventional semiconductor heterostructures, the achievement of high mobility 2DEGs has been accompanied by the observation of new phenomena: first the integer quantum Hall effect and later, in even cleaner samples, the fractional quantum Hall effect. The stronger electron interactions and spin-orbit coupling of oxide interfaces could lead to parallel or even greater discoveries of new physical phenomena, such as the fractional quantum Hall effect at low temperatures, but in many cases, this requires a sufficiently high electron mobility of oxide 2DEGs.

Another notable discovery at the oxide interface is the recent realization of a two-dimensional hole gas at $\text{SrTiO}_3/\text{LaAlO}_3/\text{SrTiO}_3$ trilayer heterostructures [see Fig. 1(d)].³⁸ In this heterostructure, a hole gas was formed in the top SrTiO_3 layer, and an electron gas was simultaneously formed at the bottom SrTiO_3 layer. This is unexpected as oxides often feature a high hole effective mass due to the localization of the O 2p orbitals forming the valence band. This normally leads to the formation of small polarons instead of p-type conductivity.³⁹ Therefore, more theoretical insights are needed to understand the hole gas at oxide interfaces to further improve the high hole mobility of the hole gas (above



1000 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at low temperatures), besides the plenty of new remarkable properties awaiting to be explored.⁴⁰

The above four paragraphs present some of the fascinating studies and perspectives on the properties of confined electron systems at oxide interfaces. A number of additional important aspects remain to be explored and call for future investigations as follows:

- Explore the properties of the novel state where electrons are paired but remain non-superconducting.
- Control and investigate the properties of the ferroelastic domain walls.
- Investigate the quantum transport of a SrTiO_3 quantum well with a single or few conducting subbands.
- Understand, tailor, and use the hole gas in SrTiO_3 .
- Understand the role of defects in SrTiO_3 and move towards deliberate “defect engineering.”

At high temperatures, oxide interfaces keep providing fascinating phenomena and novel states, some of which are far away from the properties of their constitutive materials. Recent findings are expanding the horizon of our knowledge, giving evidences that the defective ionic interface provides opportunities to explore a new generation of technologies for information and energy applications.^{41–43} This is especially

the case for metal oxides, where a prominent transport of oxygen defects and ions leads to both purely ionic-electronic conductivity and mixed ionic-electronic conductivity (MIEC). Such charge transport effects are the result of both structural and electrical point defects in the crystal structure that are controlled by the ionic charge balance as well as by thermodynamical conditions at the operation environment.⁴² Currently, these ionic materials find application both as bulk and thin films in advanced energy systems such as in catalysis and electrochemical-driven power-to-chemical conversion devices.^{44–46} Moreover, impressive electro-chemo-mechanical properties have been recently disclosed, both at high and low temperatures, opening up to a new paradigm for MEMS and lead-free actuation technologies.^{47,48}

When two defective oxides are in intimate contact, e.g., after forming highly coherent interfaces of alternating layers, charge redistribution or mass transfer of ions may happen at the interface, leading to the possibility of enhancing the ionic conductivity or stabilizing phases and defects which are otherwise not accessible.^{49,50} In such conditions, defects and interface properties are strongly interlinked as additional energetic surface content, tunable stress-strain configurations, high defect densities, and broken symmetries of the crystals can easily induce formation of special, and sometimes

unexpected, properties which are not achievable in the bulk.⁵¹ Such properties are more dominant in nanoscale oxide systems with a high degree of structural, microstructural, and compositional control.

For nano-confined ionic conductors, i.e., *nanoionics*, several examples of enhanced properties have been reported in the literature.^{52,53} Here, nanoionic materials can enhance their conductivity either via space charge regions, forming high concentrations of mobile point defects at the near interface, or via structural lattice mismatch that is induced by matching dissimilar structures.⁵¹ In particular, the effect on conductivity is very pronounced in oxide heterostructures, where the space charge region is very narrow and the lattice mismatch repetition plays a dominant role in the overall ionic conductivity.⁵²

Despite this basic knowledge and the extensive work already done in this field, several aspects related to the control, prediction, and use of interfacial properties remain to be disclosed. Here, we treat some of the most relevant ones such as vertically aligned nanostructures (VANs) and planar heterostructures (Fig. 2).

The spatial configuration of the interfaces in nano-confined ionic materials is of great relevance for the final properties and for their final applications. Currently, the most explored configuration is the planar multi-layered heterostructure. This is used for a wide range of technologies utilizing electronic devices such as memristors and all-oxide electronics as well as solid oxide fuel cells, oxide membranes, batteries, and capacitors. A less studied configuration is the VANs. The VANs grow typically via self-assembly using PLD, starting by the nucleation of the preferred phases on the surface followed by the growth of the lowest Gibbs free energy phases in the composite in a vertically epitaxial way.⁵⁴ The ability to synthesize vertically straight structures along the direction of the deposition is fascinating from both a fundamental and technological perspective. Vertically aligned hetero-interfaces can be used to induce ionic conductivities which are much higher than that of laterally

plain films^{55,56} and to explore new physical phenomena in the directions along and perpendicular to the vertical interfaces. Recent results show that VANs hold great promise for high density memory devices⁵⁷ and for electrochemical oxygen redox cycles for high temperatures fuel cells.^{58,59} Furthermore, the in-plane strain can be independently controlled from the out-of-plane strain at the vertical structures, which adds another degree of freedom to tailor the properties of these heterostructures compared to the standard planar heterostructures. In solid oxide fuel cells, for example, VANs have been used to give sufficiently fast electrolyte diffusion as well as sufficiently fast cathodic reactions⁶⁰ by assembling pure ionic conductors with MIECs, i.e., Gd-doped $\text{CeO}_2\text{-(La,Sr)CoO}_3$, both as dense and porous layers.^{60,61} In another relevant VAN design, a high performing electrochemical capacitor has been proposed to tune electrostatic effects at the boundary in Pr-doped ceria,⁶² suppressing space charge region effects at low temperatures.

It has long been known that the size of the system plays a major role in the properties of the materials. A substantial increase of the ionic conductivity was already illustrated when the thickness of individual layers was decreased down to the nanometric region in oxide superlattices, where the space charge regions are comparable to the layer thickness.^{51,63,64} This is, e.g., the case for multilayers of yttria-stabilized zirconia (YSZ) and CeGdO_2 (CGO), which showed that as the layer thickness decreased, the overall ionic conductivity of the system first increased to a maximum and afterwards decreased again.⁶⁵ The subsequent decrease in the ionic conductivity was attributed to the possible intermixing at the interfaces when the layers became too thin.

Electro-chemo-mechanical systems in acceptor/donor doped- CeO_2 and stabilized- Bi_2O_3 phases are also excellent examples. Electromechanical properties of these two materials are linked to the defect concentration and mobility, e.g., of either mobile or frozen oxygen defects. These two cases well match novel theories about retained disorder and broken symmetries.⁶⁶⁻⁶⁸

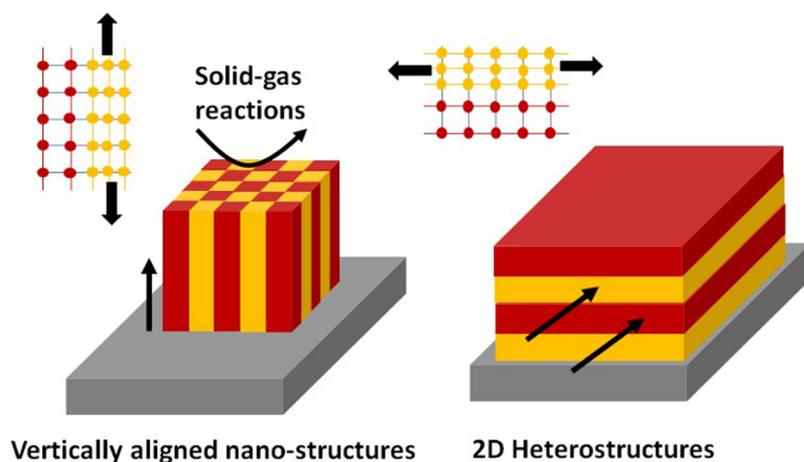


FIG. 2. Schematic diagrams of a different type of nanocomposite thin films: vertically aligned nanostructures and planar oxide multilayers.

Frozen defective ionics have recently shown that gigantic electrostrictive properties can even exist in centrosymmetric defective metal oxides as a result of defect-induced local distortions of the lattice.⁴⁷ The option to tune the defect concentration by nano-confinement is still unexplored and can lead to novel designs of MEMS and electrochemical actuators. This also includes electromechanical actuation, as for nano-metric PrCeO₂/YSZ electrochemical cells at high temperatures (>500 °C). When nano-confined, such thin film-based electrochemical cells can in principle lead to fast electrochemical redox cycles at the highly defective interface even under conditions of low charge mobility, as is expected for ionic conductors operating at room temperatures.⁶⁹

Achieving novel thermodynamic configurations for fast ionic conductors, which can even be stabilized in the absence of structurally stabilizing dopants, can be used to create new functions and boost the research towards novel technologies, including energy microelectronics, ionotronics, and neuromorphic devices. The possibility to synthesize metastable oxide materials in off-equilibrium conditions⁷⁰ are attractive since metastable compounds may have high performance and peculiar properties not observed in their thermodynamically stable counterparts.^{49,64} The confinement of metastable structures provides a strategy to design and stabilize new materials that are comprised of intrinsically unstable but high-performing component materials. In recent studies on BiO_x, it was shown that an exceptionally high chemical stability is achieved under reducing conditions and redox cycles at high temperatures, usually unattainable for the constitutive oxide materials. Even more interestingly, at low oxygen partial pressure, the layered material shows anomalous high conductivity, equal or superior to pure Bi₂O₃ in air.⁴⁹

Some of the most relevant approaches to improve the performance of ionic materials have been summarized above. The future trends in this research area can be envisaged along various directions:

- Tune the vertical heterostructures to achieve a similar control as what we already have for the planar ones. Such a goal is far from being reached, and a better understanding of the growth mechanism is still required.
- Investigate surfaces and interfaces using *in situ* impedance measurement during the sample synthesis.⁷¹
- Understand the effect of the epitaxial strain associated with the mismatch between two materials, the role of defects, and how these relate to the ionic conductivity.
- Understand in detail the two factors, which determine the VAN growth: thermodynamics and kinetics. They both influence the VAN growth in a quite complicated way and are not yet fully understood.

By combining the electronic and ionic migration of charges, a new area emerged: ionotronics. This field takes advantage of combining the benefits of both electronic and ionic properties. This can particularly be the case when considering moveable ionic species such as oxygen vacancies,

which also act as n-type dopants in many oxides.^{53,72} The formation or diffusion of oxygen ions may occur across an interface, in particular during growth, and tuning the oxygen affinity of one of the constituent materials can thus be used as a convenient handle to control this mass transport.⁷ The driving force for oxygen ion diffusion may also be applied to electric fields as the case in many memristive devices.^{53,72}

Memristive devices are a good example illustrating the use of ionotronics and nanoionics in information related devices. Recently, memristive devices have attracted great attention as potential high-density memory devices and for neuromorphic computation. These are components that change their electric resistance upon the application of an electric field and retaining (remembering) the new resistance once the electric field is switched off. The change in the resistance often occurs due to the migration of oxygen vacancies in the active material. Here, a path with a high density of oxygen vacancies connects two electrodes in the low-resistive state whereas the path is broken in the high-resistive state. High oxygen ion conductivity is directly linked to fast operation in ionotronic devices such as memristors.^{53,72} Design strategies which enable controlling the conductivity of the oxygen ions would boost this technology, allowing the exploitation of all its latent advantages.

As the properties of many metal oxides can change significantly with the oxygen vacancy concentration, understanding the correlations between the oxygen content, crystal structure, and properties such as the electrical resistance is a central point for designing new ionotronic systems at the nanoscale. In addition, computation and experimental material design can be used to screen for advantageous material combinations both via Density Functional Theory calculations and experimental approaches combined with big data mining, artificial intelligence, and machine learning. When appropriate materials are identified, one can build up ionotronic networks designed from, e.g., memristive components where the properties of the components can evolve and improve over time. In this way, one can design computers where the hardware itself can be improved according to the tasks needed to be solved. This mimics the process of the human brain when it matures from its infant state to the powerful and energy efficient computer it becomes inside an adult.

Interfaces between two oxides can exhibit properties markedly different from the parent materials, leading to fascinating electronic, ionic, and ionotronic properties. Electronically, oxide interfaces, particularly the LaAlO₃/SrTiO₃ heterostructure, have served as a versatile playground, leading to the discovery of electron pairing in the absence of superconductivity, multifunctional domain wall physics, enhanced electron mobility, and simultaneous hole and electron conduction. In addition, interfaces can be used to greatly enhance the ionic conductivity and chemically stabilize high-conducting phases, and planar as well as vertical interfaces each find their merits. By combining the electronic and ionic properties, one can harvest the benefits of ionotronics, as in the

cases of electro-chemo-mechanical systems and typical memristive devices, where the electronic charge flow is closely coupled to the ionic electromigration. Particular attention has to be paid to the detailed understanding of the separation of the ionic vs electronic contributions under relevant operating conditions, which has so far been lacking care. Nonetheless, as the gap between electronic and ionic oxide interfaces is closing, many fascinating properties and applications are expected.

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