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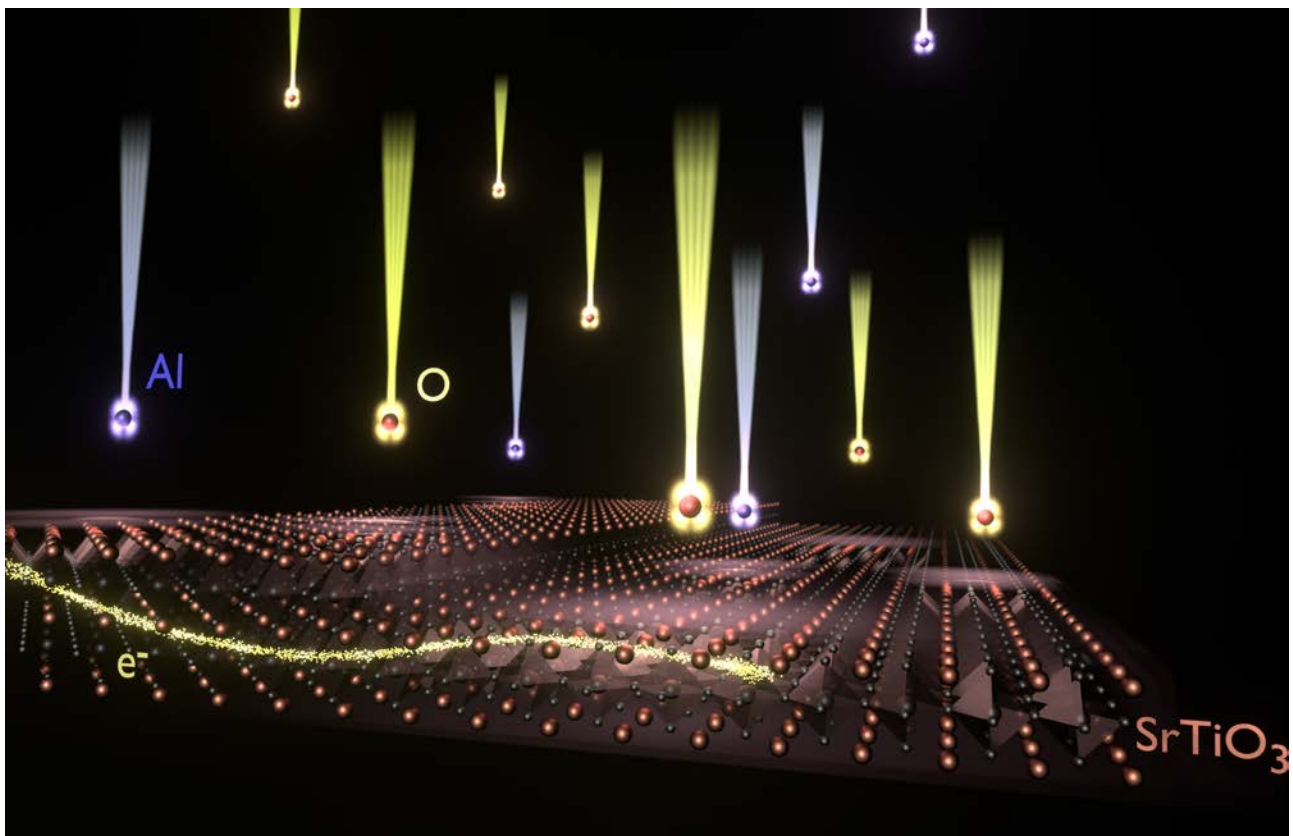
Perspectives on Oxide Heterostructures – The Curious Case of γ -Al₂O₃/SrTiO₃

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Abstract

The heterostructure formed by depositing nanoscale thin films of spinel γ -Al₂O₃ on perovskite SrTiO₃ exhibits a range of exciting properties including room temperature epitaxial growth, high electron mobility, strain-tunable magnetic order, and a symmetry-related reordering of the conduction bands. In comparison to the benchmark LaAlO₃/SrTiO₃ heterostructure, the γ -Al₂O₃/SrTiO₃ heterostructure has been more sparsely investigated, which leaves plenty of room for scientific and technological discoveries. In this perspective article, I describe the key findings of the γ -Al₂O₃/SrTiO₃ heterostructure and propose five directions for future research: 1) an exploration of novel phenomena emerging when relaxing the conventional epitaxial constraint of matching crystal structures across the interface, 2) a dynamic switching of a strong polarization through nanoscale electromigration of aluminum vacancies, 3) autonomous and forced enhancement of the electron mobility via oxygen vacancy diffusion, 4) writing and erasing of magnetic and conducting nanolines using ferroelastic domain walls, and 5) a multiferroic state formed by combining ferroelectricity, ferromagnetism, and ferroelasticity. The proposed research directions may shed light on both fundamental aspects of the heterostructure and pave the way for applications within green energy devices and nanoelectronics.



The strong market pull for high-speed and power-saving electronics has fueled the tremendous development in realizing faster, smaller, and more energy-efficient nanoelectronic devices. Two routes are used to satisfy this market pull: (i) Improving existing devices or (ii) designing devices with new functionalities. Appealing functionalities may be realized by using materials beyond the semiconducting materials that currently constitute the backbone of state-of-the-art electronic devices. A key example is the emergence of neuromorphic computation where non-volatile changes in the resistance observed on the nanoscale in, e.g., memristive oxides can be used to form a computational framework inspired by the human brain, which features both improved energy efficiency, learning capabilities and suitability for deep learning tasks [1]. A material system particularly rich in novel functionalities is the oxide heterostructure formed by depositing a nanoscale thin film of LaAlO_3 epitaxially on SrTiO_3 [2]. Despite both oxides being considered non-magnetic and insulating, conductivity and magnetism emerge at the interface along with numerous other functionalities [3]. In the wake of the large interest in the $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructure, a new artificial system was obtained by replacing perovskite LaAlO_3 with spinel $\gamma\text{-Al}_2\text{O}_3$ [4]. The $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$ heterostructure has shown to be an astonishing material platform in many ways, yet, the heterostructure has been much less studied compared to the benchmark $\text{LaAlO}_3/\text{SrTiO}_3$, which leaves plenty of room for future research adventures. Nonetheless, the heterostructure has already proven to possess several exciting properties not observed in the $\text{LaAlO}_3/\text{SrTiO}_3$ counterpart or in other SrTiO_3 -based heterostructures. In this perspective article, I will first highlight some of the key findings that make the $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$ heterostructure an exciting material platform to study, and secondly discuss several key opportunities for future research within nanoscale tailoring of this heterostructure.

Key findings:

Synthesis and electrical conductivity of $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$:

The first remarkable characteristic of the $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$ heterostructure is the possibility to grow the spinel $\gamma\text{-Al}_2\text{O}_3$

epitaxially on cubic perovskite SrTiO_3 using e.g. pulsed laser deposition and atomic layer deposition [5–7]. Typically, thin films of $\gamma\text{-Al}_2\text{O}_3$ with a thickness below 10 nm are deposited [5–7]. Despite the materials having different crystal structures, the oxygen sub-lattices are highly compatible, which enables the non-isomorphic epitaxial growth, even when depositing $\gamma\text{-Al}_2\text{O}_3$ at room temperature with pulsed laser deposition [4]. The matching oxygen sublattices are displayed in Figure 1a, which depicts SrTiO_3 capped with a generic spinel structure AB_2O_4 where aluminum occupies both A and B sites in the case of $\gamma\text{-Al}_2\text{O}_3$. The symmetry breaking at the spinel/perovskite interface is central to understanding the interface properties. For instance, when electrically insulating $\gamma\text{-Al}_2\text{O}_3$ is deposited on the insulating SrTiO_3 , the resulting $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$ heterostructure becomes conducting, and the itinerant electrons are confined at the interface by virtue of the broken symmetry [4,8]. The itinerant electrons confined to the interface live in a band structure that differs significantly from other SrTiO_3 -based heterostructures due to the broken lattice symmetry [9,10]. From annealing in oxygen [11], high-temperature equilibrium conductance experiments [12], and numerical modeling [13] it is deduced that the itinerant electrons originate from oxygen vacancy donors formed in SrTiO_3 during the deposition. Hence, the origin of the itinerant electrons shares similarities to other SrTiO_3 -based systems where amorphous or metal top layers such as Al are deposited on SrTiO_3 [14–16]. This origin raises an interesting paradox: The high-temperature equilibrium conductance measurements attribute the interface conductivity in $\text{LaAlO}_3/\text{SrTiO}_3$ to the LaAlO_3 polarity, but this is not the case for $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$ although $\gamma\text{-Al}_2\text{O}_3$ has been considered polar [12]. Revisiting the atomic structure of $\gamma\text{-Al}_2\text{O}_3$, it was deduced that $\gamma\text{-Al}_2\text{O}_3$ can be non-polar for particular distributions of the aluminum vacancies that are intrinsically present in $\gamma\text{-Al}_2\text{O}_3$ [17].

Tunable electronic properties of $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$:

Using the understanding of how the conductivity arises in $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$, the carrier density can be tuned by controlling the oxygen vacancy concentration by varying the $\gamma\text{-Al}_2\text{O}_3$ deposition parameter [18] or performing post-annealing in oxygen at temperatures below 300 °C [11]. A similar tunability through defect engineering was also found in the heterostructure

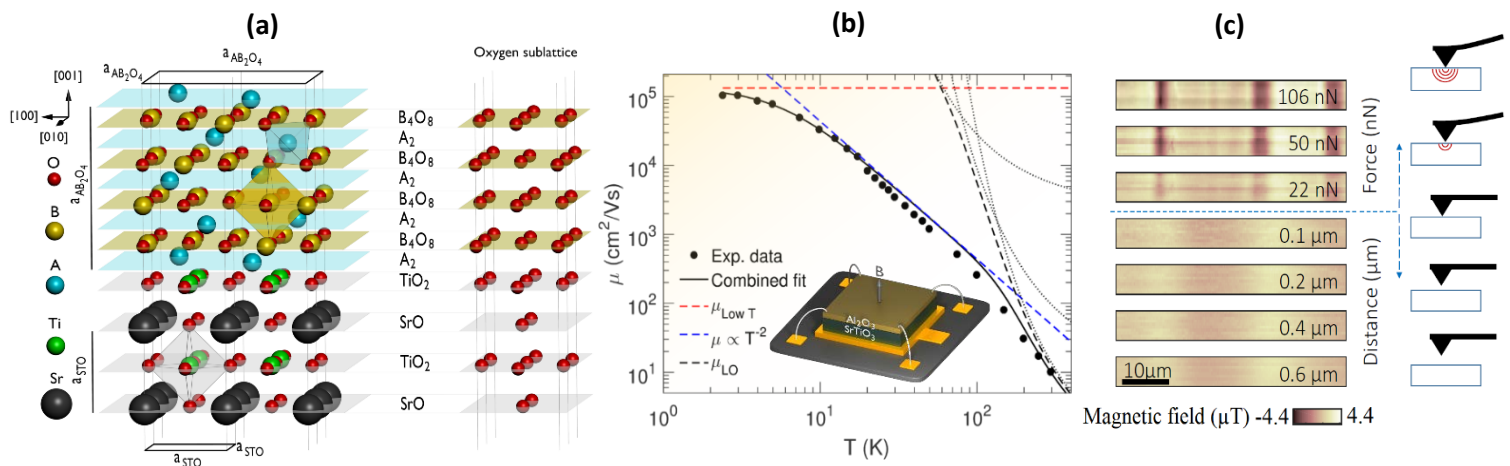


Figure 1 – Properties of the $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$ heterostructure: (a) Schematics of the crystal structure of the spinel/perovskite heterostructure where both A and B sites are occupied by aluminum with $2^{2/3}$ aluminum vacancies pr. unit cell in the case of $\gamma\text{-Al}_2\text{O}_3$. Despite the different crystal structures, $\gamma\text{-Al}_2\text{O}_3$ can grow epitaxially on SrTiO_3 due to the compatible oxygen sublattice as depicted on the right-hand side. (b) Electron mobility (μ) as a function of temperature (T) including a fit using three different scattering contributions. (c) Scanning SQUID maps of the stray magnetic field above the $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$ surface arising from magnetic order in the heterostructure as the probe is scanned in non-contact mode (lower 4 panels) and in contact mode with increasing pressure (upper 3 panels). The figures 1b and 1c are adapted from Ref. [21] and [21] with permission from American Physical Society and Springer Nature, respectively.

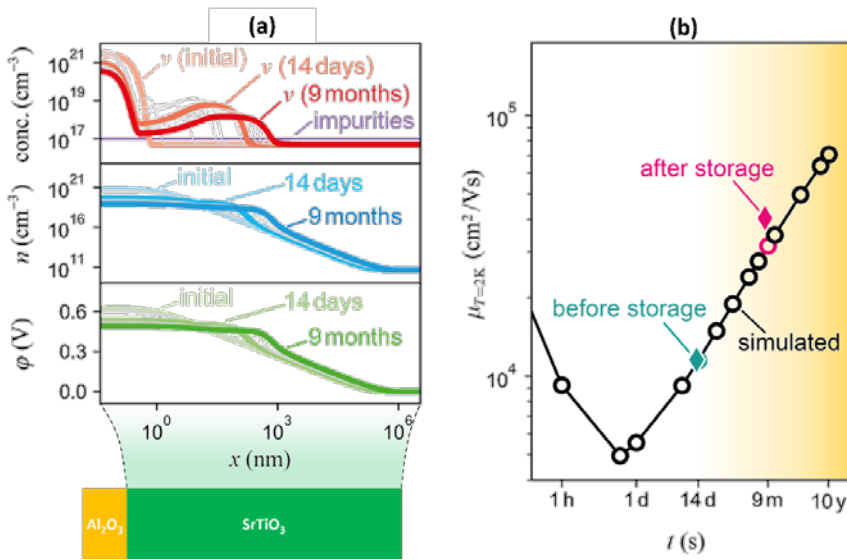


Figure 2 – Self-enhancing electron mobility: (a) Simulated depth-distribution of oxygen vacancy donors and background impurities (top) as well as itinerant electrons (middle) in a γ -Al₂O₃/SrTiO₃ heterostructure stored at room temperature for different periods after deposition. Here, x denotes the distance from the γ -Al₂O₃/SrTiO₃ interface. The electrostatic potential (bottom) associated with the oxygen vacancy distribution, which governs the distribution of itinerant electrons. (b) Simulated and measured electron mobility at 2 K ($\mu_{T=2K}$) for various storage times (t) after deposition of the γ -Al₂O₃/SrTiO₃ heterostructure. The figure are adapted from Ref. [25] with permission from American Physical Society.

composed of amorphous LaAlO₃ deposited on SrTiO₃ where the electrons also originate from oxygen vacancies [11]. Electrons can also be induced in a non-volatile fashion using external stimuli on the macroscopic scale through conventional electrostatic gating [18], ionic liquid gating [19] or light exposure [18,20], and on the nanoscale using a biased atomic force microscopy tip [11]. The latter allows for a versatile patterning of circuits with nanoscale resolution [11].

Mechanically tunable magnetism:

Surprisingly, γ -Al₂O₃/SrTiO₃ was found to possess a mechanically tunable magnetic state [21]. The magnetic state manifests itself at $T < 40$ K both via the anomalous Hall effect and a magnetoresistance that deviates from Kohler's rule. Scanning SQUID was further used to detect a magnetic order extending hundreds of micrometers with modulations occurring along the tetragonal domain walls of SrTiO₃ (see Figure 1c). Applying force on the γ -Al₂O₃/SrTiO₃ surface using the scanning SQUID changes the magnetic order drastically, resulting in much stronger modulations (see Figure 1c). It was speculated that the applied force enhanced the magnetization by shifting the balance between the competition of a ferromagnetic order and a non-magnetic order. The ferromagnetic order is likely to arise from localized magnetic moments on oxygen vacancies that exchange couple to the itinerant electrons. The non-magnetic order may originate from, e.g., a singlet electron pairing as observed in a non-superconducting state for other SrTiO₃-based heterostructures [22–24].

Electron mobility:

At room temperature the electron mobility in γ -Al₂O₃/SrTiO₃ is generally found to be limited to 12 cm²/Vs by phonon scattering [25], but with a few reports stating values exceeding 30 cm²/Vs [26,27]. At 2 K the mobility exceeds 100,000 cm²/Vs (see Figure 1b) at a high carrier density of $\sim 5 \cdot 10^{14}$ cm⁻² [4,25], which differs fundamentally from bulk conducting SrTiO₃ and most other SrTiO₃-based heterostructures where high mobility is found at low carrier densities [28]. This mobility value at low temperatures is amongst the highest obtained for oxides [28].

The mobility in γ -Al₂O₃/SrTiO₃ can be enhanced by gentle post-annealing at ~ 100 °C or during prolonged room temperature storage [29]. The finite mobility of oxygen vacancies – acting both as electron donors and scattering centers – was attributed to being the cause of this self-enhancing mobility [13]. Drift-diffusion calculations were performed to describe the oxygen vacancy movement (see Figure 2). Here, part of the oxygen remained fixed at the γ -Al₂O₃/SrTiO₃ interface due to the broken lattice symmetry, whereas other oxygen vacancies formed a diffusion front that moved gradually deeper into the bulk of SrTiO₃ due to electrostatic repulsion (Figure 2a). The simulations further show that the resulting electrostatic potential from the charged oxygen vacancies caused a significant fraction of the electrons to be distributed between the interface and the diffusion front, thereby forming a high-way for high-mobility conduction in between the regions of high oxygen donor concentrations. A resulting self-enhancing electron mobility was predicted, which matched the experimental data well (Figure 2b). The high carrier density of $\sim 5 \cdot 10^{14}$ cm⁻² is therefore predicted to be accompanied by a nanometric electron depth distribution after deposition to extending a micrometer or more into the SrTiO₃ substrate after prolonged aging for several months. This can be compared to experimental depth distributions extending 0.9 nm and 7.5 nm into SrTiO₃ as deduced from angle-dependent x-ray photoemission spectroscopy at room temperature and cryogenic infrared ellipsometry performed on samples without prolonged aging [4,8].

Future perspectives:

In contrast to the prototypical perovskite/perovskite LaAlO₃/SrTiO₃ interface, the spinel/perovskite γ -Al₂O₃/SrTiO₃ interface has been investigated more sparsely, which leaves plenty of room for exploring how the altered crystal structure across the interface may lead to unexpected phenomena. Below, I outline five key opportunities for future research inspired by the current knowledge of the γ -Al₂O₃/SrTiO₃ heterostructure:

for the construction of stacked heterostructures. Of particular interest is the formation of conducting interfaces in heterostructures formed by stacking individual membranes. As the mechanism for forming conductivity in epitaxially grown γ - $\text{Al}_2\text{O}_3/\text{SrTiO}_3$ relies on the movement of oxygen across the interface, kinetic limitations may prevent conducting interfaces to be formed by room temperature stacking of non-conducting γ - Al_2O_3 and SrTiO_3 membranes. In contrast, conductivity may be formed by high-temperature reduction of SrTiO_3 , which forms oxygen vacancy donors that can be kinetically trapped inside SrTiO_3 by a protective layer of γ - Al_2O_3 . The new γ - $\text{Al}_2\text{O}_3/\text{SrTiO}_3$ interface may also serve to localize and thermodynamically stabilize oxygen vacancies at the interface.

Thickness-dependent dynamic polarity switching:

Beyond the potential polarity formed at the interface in γ - $\text{Al}_2\text{O}_3/\text{SrTiO}_3$, polarity may also form within the γ - Al_2O_3 layer. To obtain charge neutrality in γ - Al_2O_3 , each spinel unit cell intrinsically contains $2^{2/3}$ aluminum vacancies ($\text{Al}_{21/3}\text{O}_{32}$) located on lattice sites with tetragonal and/or octahedral symmetries (see Figure 1a). Depending on the film thickness of γ - Al_2O_3 as well as the distribution of aluminum vacancies in γ - Al_2O_3 , the film may either be highly polar or overall non-polar (Figure 3). By distributing the aluminum vacancies freely on tetragonal or octahedral sites, it was shown that no distributions of aluminum vacancies exist that give a non-polar film for thicknesses below one unit cell (0.8 nm corresponding to 8 sublayers) [4]. This should be compared to RHEED-monitored growth with sub-unit cell control of the thickness as 4 RHEED oscillations correspond to a single unit cell [4]. For a γ - Al_2O_3 thickness of 1 unit cell, the aluminum vacancies can either distribute in ways that produce a strong polarity (Figure 3c-d) or no overall polarity (Figure 3e-f) with a large predicted impact on the associated electrostatic potential build-up in the γ - Al_2O_3 layer (Figure 3g). A strong polarization of $75 \mu\text{C}/\text{cm}^2$ is expected for aluminum vacancies distributed according to Figure 3c, which exceeds that found in single crystals of the strongly polar material BaTiO_3 ($\sim 25 \mu\text{C}/\text{cm}^2$ [37]) as well as the spontaneous polarization at the surface of single-crystalline SrTiO_3 substrates ($\sim 5 \mu\text{C}/\text{cm}^2$ [38]). A yet untested hypothesis exists suggesting that the polarity in γ - Al_2O_3 might be tunable by electric fields due to the electromigration of aluminum ions [17]. If disregarding the internal electrostatic build-up associated with the various cation configurations, the movement of aluminum vacancies is expected to have an activation barrier on the order of 0.6 eV for moving aluminum vacancies between lattice sites within γ - Al_2O_3 [39]. This is on the same order of magnitude as the barrier for oxygen vacancy diffusion in SrTiO_3 where electromigration is commonly observed [40,41]. This would offer switchable functionalities with similarities to conventional ferroelectrics, but with the switching caused by large-scale defect migration rather than small polar lattice distortions within a unit cell. In addition, the polarity may also be sensitive to applied stress and temperature, resulting in piezoelectric and pyroelectric properties.

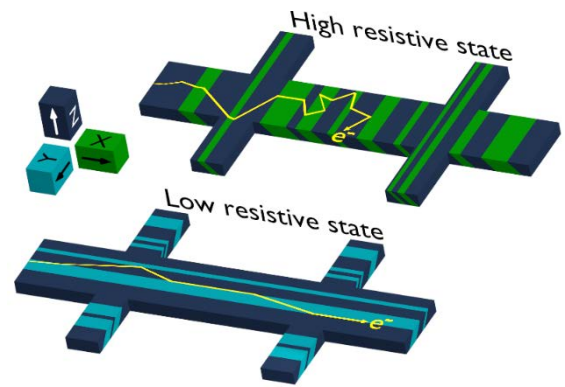


Figure 5 – Ferroelastic domain wall memristor: Schematics of a ferroelastic domain wall memristor where external stimuli such as stress or electric fields may be used to control the landscape of ferroelastic domain walls and hence the resulting electrical resistivity in a non-volatile fashion.

Self-enhancing electron mobility:

Oxygen vacancies in γ - $\text{Al}_2\text{O}_3/\text{SrTiO}_3$ serve key roles as electron dopants, scattering sites limiting the low-temperature mobility, and a likely source for magnetism. The diffusivity of oxygen vacancies in SrTiO_3 with an energy barrier on the order of 0.6 eV makes it possible for these key defects to move in absence of high temperatures. This stands in stark contrast to conventional electronic systems where donors are typically static, and it, therefore, opens up opportunities to tune functional properties through post-deposition treatment [11,42]. As mentioned above, it was suggested that the autonomous rearrangement of oxygen vacancies at room temperature resulted in a depth distribution, which favors high-mobility carriers [13]. One may expect that the diffusion can be changed from autonomous to controlled on-demand by adding an electric field from electrostatic gates to control the electromigration of oxygen vacancies. In this way, one can envision a dynamic control of both the location of electron donors as well as the resulting confinement potential and electron distribution in a non-volatile fashion. Back-gates are expected to primarily modulate the depth distribution of donors and vacancies whereas side gates or local gates from probes may control the lateral distribution as well. This is expected to have a strong impact on the electron mobility as well as other functional properties such as the magnetism observed in γ - $\text{Al}_2\text{O}_3/\text{SrTiO}_3$. The γ - $\text{Al}_2\text{O}_3/\text{SrTiO}_3$ interface here is expected to play the particular role of partially trapping the oxygen vacancies near the broken interface, which may be enhanced or diminished by replacing the γ - Al_2O_3 layer with other top films such as amorphous top layers [14], spinel layers with cation substitutions [43] or metal layers [16] to form a set of oxygen-deficient SrTiO_3 -based heterostructures.

Writing functionalities with structural domain walls:

The magnetism and current distribution in γ - $\text{Al}_2\text{O}_3/\text{SrTiO}_3$ have stripy modulations at cryogenic temperatures aligned along the [100], [010], and [110] crystal directions [21,25]. The stripy features are attributed to the ferroelastic domains arising when SrTiO_3 transitions from cubic to tetragonal around 105 K. The

transition forms three different domains where the elongation of the tetragonal unit cell is along the x -, y -, and z -direction, respectively. This leads to a distribution of domains separated by domain walls where the spatial differences in the lattice here form modulations of the electronic and magnetic properties [21,25]. The size, number, and spatial distribution of domains and domain walls can be controlled using external stimuli such as mechanical stress and electric fields on both the macroscopic and microscopic scales [21,44]. This opens up for dynamically writing and erasing nanoscale lines with modified magnetic and conducting properties. As these lines are coupled to the underlying lattice structure, the changes are expected to be non-volatile, which may open up for designing spintronic devices and ferroelastic memristors (see Figure 5).

Multiferroicity:

As described above, SrTiO_3 turns ferroelastic below approximately 105 K. In addition, SrTiO_3 is a quantum paraelectric at cryogenic temperatures, which is characterized by the ferroelectric polarity of the unit cell being suppressed by quantum tunneling between two polar states, hence on average producing a non-polar state. As SrTiO_3 is on the verge of becoming a ferroelectric material, ferroelectricity can be induced by lattice modification such as applying stress [45], substituting Sr for Ca [46], or replacing ^{16}O with ^{18}O isotopes [47]. In addition, a ferromagnetic state appears to be formed as well in the $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$ heterostructure [21]. This suggests that a multiferroic state awaits to be discovered in $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$, which combines both ferroelastic, ferroelectric, and ferromagnetic properties in a single material system. Of particular interest would be to study to what extent the ferroelastic, ferroelectric, and ferromagnetic degrees of freedom couple together to form, e.g., magnetoelectric effects. Although this multiferroic state has yet to be observed in $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$, several studies point to an intimate coupling between the spin, lattice and charge degrees of freedom as illustrated in Figure 6. Here, the magnetization is dynamically coupled to the lattice through its strain-tunable property as well as through its modulation on ferroelastic domain walls [21]. Similarly, the charge flow is also modulated by the ferroelastic domain walls [25]. Through an electron-phonon coupling, the charge further distorts the lattice to form a polaron with an enhanced effective mass as the charge flows in the structure [10]. Lastly, the spin and charge degrees of freedom are also coupled through the anomalous Hall effect and exchange coupling of spins with the itinerant charge carriers [21]. Whereas the ways these degrees of freedom couple together are not exclusive to $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$ but rather occur in other SrTiO_3 -based material systems as well [21,44,48–53], all coupled degrees of freedom have been observed in a single $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$ sample. In addition, the coupling between charge and spin degrees of freedom through the anomalous Hall effect manifests itself in $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$ as a strongly non-linear Hall resistance below a threshold temperature, which coincides with

the emergence of a stripy modulation of the magnetic signal picked up by scanning magnetometry [21].

Conclusion:

The $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$ heterostructure has already proven to be an exciting and multifunctional material system, which is less explored compared to the archetypical $\text{LaAlO}_3/\text{SrTiO}_3$ interface. Nonetheless, replacing the LaAlO_3 film with $\gamma\text{-Al}_2\text{O}_3$ results in, e.g., a severely broken lattice symmetry, reordering of the conduction band, and high electron mobility. I here propose to further expand the range of properties by 1) investigation of heterointerfaces not bound by conventional epitaxial constraints, 2) dynamic and thickness-dependent polarity switching, 3) electromigrative control of electron donors, 4) writing and erasing of conducting and magnetic nanolines, and 5) realization of co-existing ferroelasticity, ferromagnetism, and ferroelectricity in $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$. This renders the material property an interesting material platform to explore for scientific purposes as well as for applications utilizing ferroelectricity, high-mobility electronics, and multiferroicity.

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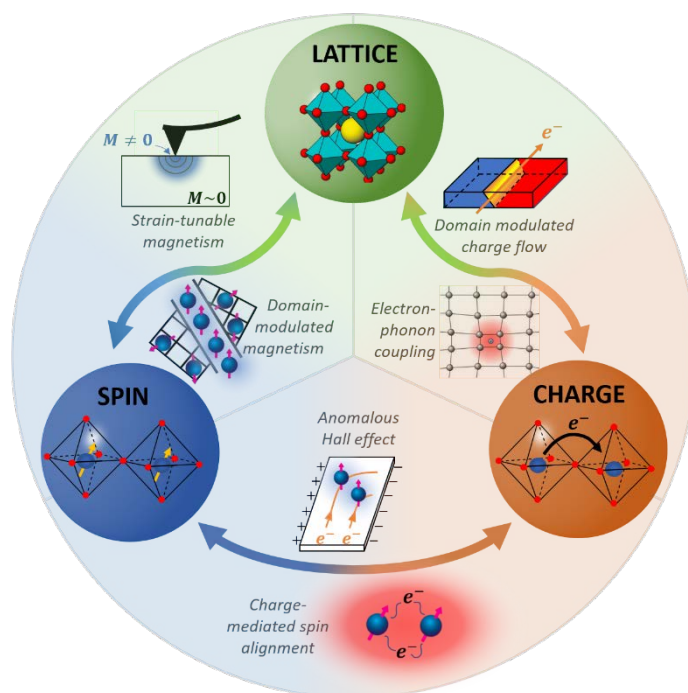


Figure 6 – Coupling of spin, lattice and charge degrees of freedom: The wide range of properties observed in $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$ arises due to the coupling of spin, lattice and charge degrees of freedom. The figure is adapted from Ref. [17] with permission from Springer Nature.

References:

- [1] D.V. Christensen, R. Dittmann, B. Linares-Barranco, A. Sebastian, M. Le Gallo, A. Redaelli, S. Slesazek, T. Mikolajick, S. Spiga, S. Menzel, I. Valov, G. Milano, C. Ricciardi, S.-J. Liang, F. Miao, M. Lanza, T.J. Quill, S.T. Keene, A. Salleo, J. Grollier, D. Marković, A. Mizrahi, P. Yao, J.J. Yang, G. Indiveri, J.P. Strachan, S. Datta, E. Vianello, A. Valentian, J. Feldmann, X. Li, W.H.P. Pernice, H. Bhaskaran, S. Furber, E. Neftci, F. Scherr, W. Maass, S. Ramaswamy, J. Tapson, P. Panda, Y. Kim, G. Tanaka, S. Thorpe, C. Bartolozzi, T.A. Cleland, C. Posch, S. Liu, G. Panuccio, M. Mahmud, A.N. Mazumder, M. Hosseini, T. Mohsenin, E. Donati, S. Tolu, R. Galeazzi, M.E. Christensen, S. Holm, D. Ielmini, N. Pryds, 2022 roadmap on neuromorphic computing and engineering, *Neuromorph. Comput. Eng.* 2 (2022) 022501. <https://doi.org/10.1088/2634-4386/ac4a83>.
- [2] A. Ohtomo, H.Y. Hwang, A high-mobility electron gas at the $\text{LaAlO}_3/\text{SrTiO}_3$ heterointerface, *Nature*. 427 (2004) 423–426.
- [3] J.A. Sulpizio, S. Ilani, P. Irvin, J. Levy, Nanoscale Phenomena in Oxide Heterostructures, *Annual Review of Materials Research*. 44 (2014) 117–149. <https://doi.org/10.1146/annurev-matsci-070813-113437>.
- [4] Y.Z. Chen, N. Bovet, F. Trier, D.V. Christensen, F.M. Qu, N.H. Andersen, T. Kasama, W. Zhang, R. Giraud, J. Dufouleur, T.S. Jespersen, J.R. Sun, A. Smith, J. Nygård, L. Lu, B. Büchner, B.G. Shen, S. Linderöth, N. Pryds, A high-mobility two-dimensional electron gas at the spinel/perovskite interface of $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$, *Nature Communications*. 4 (2013) 1371. <https://doi.org/10.1038/ncomms2394>.
- [5] Y.Z. Chen, N. Bovet, T. Kasama, W.W. Gao, S. Yazdi, C. Ma, N. Pryds, S. Linderöth, Room Temperature Formation of High-Mobility Two-Dimensional Electron Gases at Crystalline Complex Oxide Interfaces, *Advanced Materials*. 26 (2013) 1. <https://doi.org/10.1002/adma.201304634>.
- [6] M. von Soosten, D.V. Christensen, C.-B. Eom, Thomas.S. Jespersen, Y. Chen, N. Pryds, On the emergence of conductivity at SrTiO_3 -based oxide interfaces – an in-situ study, *Sci Rep.* 9 (2019) 18005. <https://doi.org/10.1038/s41598-019-54463-w>.
- [7] T.Q. Ngo, N.J. Goble, A. Posadas, K.J. Kormondy, S. Lu, M.D. McDaniel, J. Jordan-Sweet, D.J. Smith, X.P.A. Gao, A.A. Demkov, J.G. Ekerdt, Quasi-two-dimensional electron gas at the interface of $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$ heterostructures grown by atomic layer deposition, *Journal of Applied Physics*. 118 (2015) 115303. <https://doi.org/10.1063/1.4930575>.
- [8] M. Yazdi-Rizi, P. Marsik, B.P.P. Mallett, A. Dubroka, D.V. Christensen, Y.Z. Chen, N. Pryds, C. Bernhard, Infrared ellipsometry study of the confined electrons in a high-mobility $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$ heterostructure, *EPL (Europhysics Letters)*. 113 (2016) 47005. <https://doi.org/10.1209/0295-5075/113/47005>.
- [9] Y. Cao, X. Liu, P. Shafer, S. Middey, D. Meyers, M. Kareev, Z. Zhong, J.-W. Kim, P.J. Ryan, E. Arenholz, J. Chakhalian, Anomalous orbital structure in a spinel–perovskite interface, *Npj Quantum Materials*. 1 (2016) 16009. <https://doi.org/10.1038/npjquantmats.2016.9>.
- [10] A. Chikina, D.V. Christensen, V. Borisov, M.-A. Husanu, Y. Chen, X. Wang, T. Schmitt, M. Radovic, N. Nagaosa, A.S. Mishchenko, R. Valentí, N. Pryds, V.N. Strocov, Band-Order Anomaly at the $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$ Interface Drives the Electron-Mobility Boost, *ACS Nano*. 15 (2021) 4347–4356. <https://doi.org/10.1021/acsnano.0c07609>.
- [11] D.V. Christensen, M. von Soosten, F. Trier, T.S. Jespersen, A. Smith, Y. Chen, N. Pryds, Controlling the carrier density of SrTiO_3 -based heterostructures with annealing, *Advanced Electronic Materials*. 3 (2017) 1700026.
- [12] F. Gunkel, S. Hoffmann-Eifert, R.A. Heinen, D.V. Christensen, Y.Z. Chen, N. Pryds, R. Waser, R. Dittmann, Thermodynamic Ground States of Complex Oxide Heterointerfaces, *ACS Applied Materials & Interfaces*. 9 (2017) 1086–1092. <https://doi.org/10.1021/acsmi.6b12706>.
- [13] A.F. Zurhelle, D.V. Christensen, S. Menzel, F. Gunkel, Dynamics of the spatial separation of electrons and mobile oxygen vacancies in oxide heterostructures, *Phys. Rev. Materials*. 4 (2020) 104604. <https://doi.org/10.1103/PhysRevMaterials.4.104604>.
- [14] Y. Chen, N. Pryds, J.E. Kleibeuker, G. Koster, J. Sun, E. Stamate, B. Shen, G. Rijnders, S. Linderöth, Metallic and Insulating Interfaces of Amorphous SrTiO_3 -Based Oxide Heterostructures, *Nano Letters*. 11 (2011) 3774–3778. <https://doi.org/10.1021/nl201821j>.
- [15] Q. Fu, T. Wagner, Metal/Oxide Interfacial Reactions: Oxidation of Metals on SrTiO_3 (100) and TiO_2 (110), *The Journal of Physical Chemistry B*. 109 (2005) 11697–11705. <https://doi.org/10.1021/jp050601i>.
- [16] D.C. Vaz, E. Lesne, A. Sander, H. Naganuma, E. Jacquet, J. Santamaria, A. Barthélémy, M. Bibes, Tuning Up or Down the Critical Thickness in $\text{LaAlO}_3/\text{SrTiO}_3$ through In Situ Deposition of Metal Overlayers, *Adv. Mater.* 29 (2017) 1700486. <https://doi.org/10.1002/adma.201700486>.
- [17] D.V. Christensen, A. Smith, Is $\gamma\text{-Al}_2\text{O}_3$ polar?, *Applied Surface Science*. 423 (2017) 887–890. <https://doi.org/10.1016/j.apsusc.2017.06.184>.

- [18] D.V. Christensen, F. Trier, M. von Soosten, G.E.D.K. Prawiroatmodjo, T.S. Jespersen, Y.Z. Chen, N. Pryds, Electric field control of the γ -Al₂O₃/SrTiO₃ interface conductivity at room temperature, *Applied Physics Letters*. 109 (2016) 021602. <https://doi.org/10.1063/1.4955490>.
- [19] W. Niu, Y. Zhang, Y. Gan, D.V. Christensen, M. von Soosten, E.J. Garcia-Suarez, A. Riisager, X. Wang, Y. Xu, R. Zhang, N. Pryds, Y. Chen, Giant Tunability of the Two-Dimensional Electron Gas at the Interface of γ -Al₂O₃/SrTiO₃, *Nano Letters*. 17 (2017) 6878.
- [20] W. Niu, Y.-W. Fang, R. Liu, Z. Wu, Y. Chen, Y. Gan, X. Zhang, C. Zhu, L. Wang, Y. Xu, Y. Pu, Y. Chen, X. Wang, Fully Optical Modulation of the Two-Dimensional Electron Gas at the γ -Al₂O₃/SrTiO₃ Interface, *J. Phys. Chem. Lett.* 13 (2022) 2976–2985. <https://doi.org/10.1021/acs.jpcllett.2c00384>.
- [21] D.V. Christensen, Y. Frenkel, Y.Z. Chen, Y.W. Xie, Z.Y. Chen, Y. Hikita, A. Smith, L. Klein, H.Y. Hwang, N. Pryds, B. Kalisky, Strain-tunable magnetism at oxide domain walls, *Nature Physics*. 15 (2019) 269–274. <https://doi.org/10.1038/s41567-018-0363-x>.
- [22] Y.-Y. Pai, A. Tylan-Tyler, P. Irvin, J. Levy, LaAlO₃/SrTiO₃: a tale of two magnetisms, in: *Spintronics Handbook, Second Edition: Spin Transport and Magnetism, Second Edition*, n.d.
- [23] G. Cheng, M. Tomczyk, S. Lu, J.P. Veazey, M. Huang, P. Irvin, S. Ryu, H. Lee, C.-B. Eom, C.S. Hellberg, J. Levy, Electron pairing without superconductivity, *Nature*. 521 (2015) 196–199. <https://doi.org/10.1038/nature14398>.
- [24] G.E.D.K. Prawiroatmodjo, M. Leijnse, F. Trier, Y. Chen, D.V. Christensen, M. von Soosten, N. Pryds, T.S. Jespersen, Transport and excitations in a negative-U quantum dot at the LaAlO₃/SrTiO₃ interface, *Nature Communications*. 8 (2017) 395. <https://doi.org/10.1038/s41467-017-00495-7>.
- [25] D.V. Christensen, Y. Frenkel, P. Schütz, F. Trier, S. Wissberg, R. Claessen, B. Kalisky, A. Smith, Y.Z. Chen, N. Pryds, Electron Mobility in γ -Al₂O₃/SrTiO₃, *Physical Review Applied*. 9 (2018) 054004. <https://doi.org/10.1103/PhysRevApplied.9.054004>.
- [26] K.H. Gao, X.R. Ma, Q.L. Li, X.H. Zhang, J.P. Xu, Y. Sun, G. Yu, High room temperature mobility in Al₂O₃/SrTiO₃ heterostructures, *EPL*. 138 (2022) 66003. <https://doi.org/10.1209/0295-5075/ac74dd>.
- [27] M. Li, H. Yan, Z. Zhang, L. Ren, J. Zhao, S. Wang, C. Chen, K. Jin, Quasi-two-dimensional electron gas at γ -Al₂O₃/SrTiO₃ heterointerfaces fabricated by spin coating method, *Journal of Applied Physics*. 124 (2018) 145301. <https://doi.org/10.1063/1.5047585>.
- [28] F. Trier, K.V. Reich, D.V. Christensen, Y. Zhang, H.L. Tuller, Y. Chen, B.I. Shklovskii, N. Pryds, Universality of electron mobility in LaAlO₃/SrTiO₃ and bulk SrTiO₃, *Applied Physics Letters*. 111 (2017) 092106. <https://doi.org/10.1063/1.5001316>.
- [29] P. Schütz, D.V. Christensen, V. Borisov, F. Pfaff, P. Scheiderer, L. Dudy, M. Zapf, J. Gabel, Y.Z. Chen, N. Pryds, V.A. Rogalev, V.N. Strocov, T.-L. Lee, H.O. Jeschke, R. Valentí, M. Sing, R. Claessen, Microscopic origin of the mobility enhancement at a spinel/perovskite oxide heterointerface revealed by photoemission spectroscopy, *Physical Review B*. 96 (2017) 161409.
- [30] N.C. Plumb, M. Radović, Angle-resolved photoemission spectroscopy studies of metallic surface and interface states of oxide insulators, *J. Phys.: Condens. Matter*. 29 (2017) 433005. <https://doi.org/10.1088/1361-648X/aa833f>.
- [31] J.R.L. Mardegan, D.V. Christensen, Y.Z. Chen, S. Parchenko, S.R.V. Avula, N. Ortiz-Hernandez, M. Decker, C. Piamonteze, N. Pryds, U. Staub, Magnetic and electronic properties at the γ -Al₂O₃/SrTiO₃ interface, *Physical Review B*. 99 (2019). <https://doi.org/10.1103/PhysRevB.99.134423>.
- [32] T.C. Rödel, F. Fortuna, S. Sengupta, E. Frantzeskakis, P.L. Fèvre, F. Bertran, B. Mercey, S. Matzen, G. Agnus, T. Maroutian, P. Lecoeur, A.F. Santander-Syro, Universal Fabrication of 2D Electron Systems in Functional Oxides, *Advanced Materials*. 28 (2016) 1976–1980. <https://doi.org/10.1002/adma.201505021>.
- [33] D. Lu, D.J. Baek, S.S. Hong, L.F. Kourkoutis, Y. Hikita, H.Y. Hwang, Synthesis of freestanding single-crystal perovskite films and heterostructures by etching of sacrificial water-soluble layers, *Nature Materials*. 15 (2016) 1255–1260. <https://doi.org/10.1038/nmat4749>.
- [34] F.M. Chiabrera, S. Yun, Y. Li, R.T. Dahm, H. Zhang, C.K.R. Kirchert, D.V. Christensen, F. Trier, T.S. Jespersen, N. Pryds, Freestanding Perovskite Oxide Films: Synthesis, Challenges, and Properties, *Annalen Der Physik*. 534 (2022) 2200084. <https://doi.org/10.1002/andp.202200084>.
- [35] Y. Li, C. Xiang, F.M. Chiabrera, S. Yun, H. Zhang, D.J. Kelly, R.T. Dahm, C.K.R. Kirchert, T.E.L. Cozannet, F. Trier, D.V. Christensen, T.J. Booth, S.B. Simonsen, S. Kadkhodazadeh, T.S. Jespersen, N. Pryds, Stacking and Twisting of Freestanding Complex Oxide Thin Films, *Advanced Materials*. 34 (2022) 2203187. <https://doi.org/10.1002/adma.202203187>.
- [36] N. Banerjee, G. Koster, G. Rijnders, Submicron patterning of epitaxial PbZr_{0.52}Ti_{0.48}O₃ heterostructures, *Applied Physics Letters*. 102 (2013) 142909. <https://doi.org/10.1063/1.4801776>.
- [37] J. Shieh, J.H. Yeh, Y.C. Shu, J.H. Yen, Hysteresis behaviors of barium titanate single crystals based on the operation of multiple 90° switching systems, *Materials Science and Engineering: B*. 161 (2009)

- 50–54.
<https://doi.org/10.1016/j.mseb.2008.11.046>.
- [38] E. Meirzadeh, D.V. Christensen, E. Makagon, H. Cohen, I. Rosenhek-Goldian, E.H. Morales, A. Bhowmik, J.M.G. Lastra, A.M. Rappe, D. Ehre, M. Lahav, N. Pryds, I. Lubomirsky, Surface Pyroelectricity in Cubic SrTiO₃, *Advanced Materials*. (2019) 1904733.
<https://doi.org/10.1002/adma.201904733>.
- [39] S.T. Murphy, B.P. Uberuaga, J.B. Ball, A.R. Cleave, K.E. Sickafus, R. Smith, R.W. Grimes, Cation diffusion in magnesium aluminate spinel, *Solid State Ionics*. 180 (2009) 1–8.
<https://doi.org/10.1016/j.ssi.2008.10.013>.
- [40] R. Waser, R. Dittmann, G. Staikov, K. Szot, Redox-Based Resistive Switching Memories - Nanoionic Mechanisms, Prospects, and Challenges, *Advanced Materials*. 21 (2009) 2632–2663.
<https://doi.org/10.1002/adma.200900375>.
- [41] J. Delahaye, T. Grenet, Gate voltage control of the AlO_x/SrTiO₃ interface electrical properties, *Journal of Physics D: Applied Physics*. 49 (2016) 395303.
<https://doi.org/10.1088/0022-3727/49/39/395303>.
- [42] A.V. Bjørli, D.V. Christensen, R. Erlandsen, N. Pryds, B. Kalisky, Current Mapping of Amorphous LaAlO₃/SrTiO₃ near the Metal–Insulator Transition, *ACS Appl. Electron. Mater.* 4 (2022) 3421–3427.
<https://doi.org/10.1021/acsaelm.2c00264>.
- [43] Y. Zhang, Y. Gan, H. Zhang, H. Zhang, P. Norby, B. Shen, J. Sun, Y. Chen, Metallic conduction and ferromagnetism in MAI₂O₄/SrTiO₃ spinel/perovskite heterostructures (M = Fe, Co, Ni), *Applied Physics Letters*. 113 (2018) 261603.
<https://doi.org/10.1063/1.5063540>.
- [44] M. Honig, J.A. Sulpizio, J. Drori, A. Joshua, E. Zeldov, S. Ilani, Local electrostatic imaging of striped domain order in LaAlO₃/SrTiO₃, *Nature Materials*. 12 (2013) 1112–1118.
<https://doi.org/10.1038/nmat3810>.
- [45] J.H. Haeni, P. Irvin, W. Chang, R. Uecker, P. Reiche, Y.L. Li, S. Choudhury, W. Tian, M.E. Hawley, B. Craigo, A.K. Tagantsev, X.Q. Pan, S.K. Streiffer, L.Q. Chen, S.W. Kirchoefer, J. Levy, D.G. Schlom, Room-temperature ferroelectricity in strained SrTiO₃, *Nature*. 430 (2004) 758–761.
- [46] J.G. Bednorz, K.A. Müller, Sr_{1-x}Ca_xTiO₃: An XY Quantum Ferroelectric with Transition to Randomness, *Phys. Rev. Lett.* 52 (1984) 2289–2292.
<https://doi.org/10.1103/PhysRevLett.52.2289>.
- [47] M. Itoh, R. Wang, Y. Inaguma, T. Yamaguchi, Y.J. Shan, T. Nakamura, Ferroelectricity induced by oxygen isotope exchange in strontium titanate perovskite, *Physical Review Letters*. 82 (1999) 3540.
- [48] A. Vasudevarao, A. Kumar, L. Tian, J.H. Haeni, Y.L. Li, C.-J. Eklund, Q.X. Jia, R. Uecker, P. Reiche, K.M. Rabe, L.Q. Chen, D.G. Schlom, V. Gopalan, Multiferroic Domain Dynamics in Strained Strontium Titanate, *Phys. Rev. Lett.* 97 (2006) 257602.
<https://doi.org/10.1103/PhysRevLett.97.257602>.
- [49] Z. Wang, S. McKeown Walker, A. Tamai, Y. Wang, Z. Ristic, F.Y. Bruno, A. de la Torre, S. Riccò, N.C. Plumb, M. Shi, P. Hlawenka, J. Sánchez-Barriga, A. Varykhalov, T.K. Kim, M. Hoesch, P.D.C. King, W. Meevasana, U. Diebold, J. Mesot, B. Moritz, T.P. Devereaux, M. Radovic, F. Baumberger, Tailoring the nature and strength of electron–phonon interactions in the SrTiO₃(001) 2D electron liquid, *Nature Materials*. 15 (2016) 835–839.
<https://doi.org/10.1038/nmat4623>.
- [50] F. Gunkel, C. Bell, H. Inoue, B. Kim, A.G. Swartz, T.A. Merz, Y. Hikita, S. Harashima, H.K. Sato, M. Minohara, S. Hoffmann-Eifert, R. Dittmann, H.Y. Hwang, Defect Control of Conventional and Anomalous Electron Transport at Complex Oxide Interfaces, *Physical Review X*. 6 (2016) 031035.
<https://doi.org/10.1103/PhysRevX.6.031035>.
- [51] C. Cancellieri, A.S. Mishchenko, U. Aschauer, A. Filippetti, C. Faber, O.S. Barišić, V.A. Rogalev, T. Schmitt, N. Nagaosa, V.N. Strocov, Polaronic metal state at the LaAlO₃/SrTiO₃ interface, *Nature Communications*. 7 (2016) 10386.
<https://doi.org/10.1038/ncomms10386>.
- [52] B. Kalisky, E.M. Spanton, H. Noad, J.R. Kirtley, K.C. Nowack, C. Bell, H.K. Sato, M. Hosoda, Y. Xie, Y. Hikita, C. Woltmann, G. Pfanzelt, R. Jany, C. Richter, H.Y. Hwang, J. Mannhart, K.A. Moler, Locally enhanced conductivity due to the tetragonal domain structure in LaAlO₃/SrTiO₃ heterointerfaces, *Nature Materials*. (2013) 1091–1095.
<https://doi.org/10.1038/nmat3753>.
- [53] A. Joshua, J. Ruhman, S. Pecker, E. Altman, S. Ilani, Gate-tunable polarized phase of two-dimensional electrons at the LaAlO₃/SrTiO₃ interface, *PNAS*. 110 (2013) 9633–9638.
<https://doi.org/10.1073/pnas.1221453110>.