Stimulating Oxide Heterostructures: A Review on Controlling SrTiO3-Based Heterointerfaces with External Stimuli

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Published in:
Advanced Materials Interfaces

Link to article, DOI:
10.1002/admi.201900772

Publication date:
2019

Document Version
Peer reviewed version

Link back to DTU Orbit

Citation (APA):
Christensen, D. V., Trier, F., Niu, W., Gan, Y., Zhang, Y., Jespersen, T. S., Chen, Y., & Pryds, N. (2019). Stimulating Oxide Heterostructures: A Review on Controlling SrTiO3-Based Heterointerfaces with External Stimuli. Advanced Materials Interfaces, 6(21), [1900772]. https://doi.org/10.1002/admi.201900772
Stimulating oxide heterostructures
- a review on controlling SrTiO₃-based heterointerfaces with external stimuli

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Abstract:
Numerous of the greatest inventions in modern society, such as solar cells, display panels and transistors, rely on a simple concept: An external stimulus is applied to a material, and the response is then utilized. Oxides often exhibit a particular colorful palette of responses to external stimuli due to the close coupling between lattice, spin, orbital and charge degrees of freedom. In particular, oxide heterostructures where oxide thin films are deposited on SrTiO₃ have proven to be a fertile playground for material scientists, and a vast amount of interesting theoretical and experimental studies showcase the wide tunabilities of these heterostructures when subjected to external stimuli. Here, we review how the properties of SrTiO₃-based heterostructures can be changed by external stimuli using electric fields, magnetic fields, light, stress, particle bombardment, liquids, gases and temperature. The application of a single stimulus or several stimuli combined often leads to unexpected changes in properties that open up for designing new devices as well as expanding the boundaries of our understanding within fundamental science.

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1. Introduction

Oxides are an exciting class of electronic materials which share key properties with conventional semiconductors, but also bring new intrinsic functionalities that are not used in most current electronics: superconductivity, ferro-, pyro-, and piezoelectricity, ferromagnetism and multiferroicity. Among the large number of oxides, strontium titanate (SrTiO$_3$, STO) has been the center of attention in numerous studies for more than half a century. STO both serves as a popular template for epitaxial growth of oxide thin films as well as by itself exhibiting an attractive palette of properties, including a low carrier density superconducting state$^{[1,2]}$, a high electron mobility$^{[3,4]}$ and ferromagnetism$^{[5]}$.

A big leap forward was made in 2004 where it was found that when depositing insulating LaAlO$_3$ (LAO) on insulating STO, a conducting interface was formed$^{[6]}$. This spurred a large interest, and a wide range of STO-based heterostructures was soon synthesized in the wake of this discovery$^{[7–11]}$. A common feature in conducting STO-based heterostructures is that the itinerant electrons are formed on the STO side of the interface, and the heterostructures thus share the interesting properties of bulk STO. In addition, various top films can be used to enhance the functionalities of the heterostructures beyond what is observed in bulk STO. For instance, the lattice symmetry breaking at the interface confines the itinerant electrons in the vicinity of the interface rather than being spread out throughout the bulk of STO$^{[12–14]}$, which enables the field effect tuning of the interface properties.

The added top film, however, also introduces complexity, and contrary to the simpler case of bulk STO, where conductivity typically is formed by donor dopants such as Nb and oxygen vacancies, the origin of the itinerant electrons at the STO-based heterointerfaces continues to be discussed. The prevalent explanations rely on the formation of oxygen vacancies at the STO side of the interface$^{[7,15,16]}$ and a diverging potential in polar top films$^{[17]}$ that may spontaneously form defects on the top film surface$^{[18]}$.

The wide range of extraordinary properties at the STO-based heterostructures stems from the interaction between the charge, orbital, spin and lattice degrees of freedom, which may be used to create new electronic devices with properties differing from those known today. The close coupling between the various degrees of freedom also leads to significant changes in the electronic, magnetic and structural properties when applying external stimuli. Due to this sensitivity, a vast amount of theoretical and experimental studies have investigated how various external stimuli can tune the properties of STO-based material systems. Here, we review the response of these systems to the following external stimuli: electric fields, magnetic fields, light, stress as well as exposure to gas, liquids, particle bombardment and temperature changes (see schematic illustration in Figure 1-1). The review is aimed to provide a representative overview of the vast literature on applying external stimuli to STO-based heterostructures, rather than providing an exhaustive account of all studies related to application of external stimuli.
2. Electrostatic potential

This section presents one of the principal means of tuning the physical properties of STO-based heterostructures and most functional materials: electrostatic stimulus.

2.1. Electrostatic gating geometries

The transport properties and interface conductivity of STO-based heterostructures can be readily tuned by varying the deposition conditions during the growth of the top oxide thin film\[15,19–21\]. With the notable exception of interface conductivity originating from oxygen vacancies in STO\[7,22\], the conducting properties of STO-based heterostructures are generally very stable. However, it is possible to electrostatically modulate the interfacial properties of STO-based heterostructures by applying an external electric field using a gate. As electrostatic gating is the main operational principle of the electronic circuits available today, this tuning pathway is of great importance. Concerning STO-based heterostructures, electrostatic gating has been shown to allow modulation of the charge carrier density and a range of other properties such as the electron mobility, electron effective mass, Rashba spin-orbit coupling strength, superconductivity, ferromagnetism, tetragonal domain ordering, and quantum transport phenomena as described in the following subsections.

The electrostatic tuning of the STO-based heterointerface can be performed in a number of different gating configurations (see Figure 2-1). The most commonly used configuration is back-gating (Figure 2-1a) where the STO substrate serves as a gate dielectric. Global or local top-gating (Figure 2-1b,c) through the top film can be achieved either by LAO in the case of LAO/STO (or equivalent oxide overlayer) acting as gate dielectric or by inclusion of a conventional dielectric layer such as HfO\(_2\), SiO\(_2\) or Si\(_3\)N\(_4\) between the gate electrode and LAO. The conventional dielectric layer has

![Figure 2-1](image-url) Overview of the different gating configurations that allow electrostatic stimulation of the interfacial state in STO-based heterostructures. a) A global back-gate can homogeneously exert an electric field through the STO substrate. b) A global top-gate can change the interface properties through the interspaced gate dielectric, which can for instance be LAO, HfO\(_2\), SiO\(_2\) or Si\(_3\)N\(_4\). c) local top-gates or side-gates can laterally constrict the interface properties by electrostatic pinching. d) A droplet of ionic liquid can be polarized to apply a very large electric field on the STO-based heterostructures without significant leakage currents at low temperature. e) By the usage of the tip of a conducting atomic force microscope (c-AFM), nanoscale metastable gating can be performed to e.g. write and erase conducting channels.
also been replaced with a ferroelectric layer, providing an alternative way to top-gate the interface. Moreover, several studies have gated the interface by means of an ionic liquid (Figure 2-1d) dispersed on top of the STO-based heterostructure (26). The gating has even been shown possible by application of an electric field from the tip of a conducting atomic force microscope (c-AFM) (Figure 2-1e) whereupon nanosized conducting paths can be written and erased (27,28). The different gating geometries differ substantially from each other particularly because the dielectric constants separating the gate and the interface typically have very different thicknesses (a few nanometers for top layers and hundreds of micrometers for the STO substrate), but also because the dielectric constant of STO is generally much higher and is both highly temperature and electric field dependent (29,30). The back-gate voltage applied across the typically 0.5 mm thick STO is therefore often in the range from ten volts to several hundreds of volts, whereas only a couple of volts are needed for the top- and ionic liquid gating setups.

In the following sub-sections we will separately discuss the physical properties that have been shown tunable by electrostatic gating using the different gating setups shown in Figure 2-1. For convenience, we include a schematic drawing of the gating configuration and material system in the figures to easily discriminate between studies using, e.g., back-gates or ionic liquid gates. Note that this schematic drawing merely serves a rough guideline for the gating setup as the dimensions and device type (Hall-bar or van der Pauw square) may differ from what was used in the particular study.

2.2. Main effects of electrostatic gating
A broad range of physical properties has been shown tunable by electrostatic gating in STO-based heterostructures. These include: 1) carrier density and band occupation, 2) electron mobility, 3) superconductivity, 4) spin-orbit coupling, 5) magnetism, 6) local microstructure and domain walls and 7) quantum properties. Arrays of field effect devices relying on the electric field tuning of the above properties have also been fabricated (31,32). Such field effect transistors based on oxide interfaces have also been reviewed by Kornblum (33).

a) Gating of carrier density and band occupation:
A change of the charge carrier density and band occupation can occur when applying an electric field from a gate to the STO-based heterointerface (34-37). Depending on the gating geometry this electric field is often sufficiently large to induce changes in the charge carrier density of the same order of magnitude as the intrinsic as-grown value, i.e. \( \sim 3\times10^{13} \) cm\(^{-2} \). In continuation of the original discovery of interface conductivity between TiO\(_2\)-terminated STO and LAO grown by pulsed laser deposition, Thiel et al. were the first to demonstrate electrostatic gating of the LAO/STO heterointerface (38). In this seminal study, the authors found that a STO substrate with 3 unit cells (u.c.) LAO grown on top normally displayed insulating transport properties. However, by applying an electric field from a back-gate (see Figure 2-1a), it was possible to induce a reproducible bipolar and non-volatile insulator-to-metal transition both at low temperatures as well as at 300 K (see Figure 2-2b). This large change in sheet resistance was explained to occur due to a moderate modulation of the band structure. As LAO/STO heterostructures with 3 u.c. LAO are expected to be on the verge of undergoing an insulator-to-metal transition due to the polar discontinuity at the interface (17), an externally applied electric field could thus release mobile charge carriers on the order of \( \sim 3\times10^{12} \) cm\(^{-2} \). A similar accumulation and depletion of carriers was later observed in a range of other STO-based heterostructures including amorphous-LAO/STO (39,40) and \( \gamma\)-Al\(_2\)O\(_3\)/STO (GAO/STO) (41,42). The conductivity in STO-based heterostructures originates from the population of Ti 3d \( t_{2g} \) orbitals, which are energy split into non-degenerate \( d_y \) sub-bands and degenerate \( d_{x^2-y^2} \) sub-bands due to the inversion symmetry breaking and electrostatic confinement at the interface (35). Due to the different coupling orientations, the relative \( t_{2g} \) sub-band occupation dictates the overall conductivity anisotropy of the electronic system as well as more subtle interactions such as the overall Rashba coefficient discussed below. By studying the low-temperature response of magnetoresistance and Hall resistance upon application of an electric field from a back-gate, Joshua et al. found that a certain critical carrier density exists where the electronic system undergoes a Lifshitz transition from one band to two types of bands (7). This critical carrier density of \( n_c \sim 1.7\times10^{13} \) cm\(^{-2} \) (see Figure 2-3b) corresponds to a specific dopant level in STO where the higher energy sub-bands \( d_{x^2-y^2} \) become populated, and the STO quantum well transitions from displaying formal one-band nature to two-band characteristics (see Figure 2-3c), as discussed in more details in Section 3. The transition dictates the manifestation of several important physical properties of STO-based heterostructures such as the superconductivity, magnetism and spin-to-charge interconversion processes as described in the following.

![Figure 2-2](image-url) a) Schematic illustration of the device. b-c) The sheet resistance (R\(_s\)) of a LAO/STO heterostructure with 3 unit cells LAO is changed by more than four orders of magnitude at 300 K upon cycling of the back-gate potential (V\(_g\)). The figure is taken from reference (38).
The LAO/STO heterostructure has also been studied extensively by global top-gating (see Figure 2-1b). For instance, Hosoda et al. was the first to study top-gating of LAO/STO where a tuning of the carrier density in the range 0.9-2.5×10^{13} \text{cm}^{-2} was shown possible at low temperature for a top-gate potential between -1.0 V and +1.0 V\(^{[44]}\). Later the same year, Eerkes et al. reported a tuning of the carrier density at low temperature between 1.6 -2.2×10^{13} \text{cm}^{-2} for a top-gate potential of -0.3 and +0.5 V, respectively\(^{[45]}\). A wide range of carrier densities between 2.0-6.0×10^{13} \text{cm}^{-2} at 2 K have later been demonstrated by Smink et al.\(^{[46]}\) using a top-gate (see Figure 2-4).

Firstly, the authors concluded that the aforementioned critical density for the Lifshitz transition is not a universal quantity for all STO-based heterostructures as otherwise first inferred. Here, the critical density for the Lifshitz transition in the top-gated LAO/STO was found to be 2.9×10^{13} \text{cm}^{-2}\(^{[47]}\). Secondly, it was found that above the Lifshitz transition, the carrier density of lowest laying \(d_{xy}\) subbands reduces upon application of larger positive top-gate voltages due to the change in quantum well confining potential (see Figure 2-4).

In semiconductor heterostructures, the ability to spatially pattern two-dimensional electron gases (2DEGs) by local top-gating (see Figure 2-1c) has been an important tool for realizing mesoscopic...
quantum devices. Key examples are the observation of quantized conductance in lateral point-contact devices and Coulomb blockade in single- and double quantum dots[48]. In the case of STO heterostructures this functionality can be combined with the unique properties offered by these materials to realize exotic hybrid devices such as gate-tunable Josephson junctions or negative-\( U \) quantum dots[49,50].

For STO-based heterostructures several studies have investigated the application of local top-gating and, quasi-equivalently, side-gating. Goswami et al. demonstrated a successful depletion of the interface conductivity below two constricting top-gates thus leaving a narrow conducting channel with a width that could be controlled with the top-gate voltage both at 4.2 K and 300 K (see Figure 2-5)[51]. A similar depletion and lateral constriction of STO-based heterointerface conductivity have subsequently been undertaken by other studies[52–55].

![Figure 2-5](image)

**Figure 2-5** a) Schematic illustration of the gating configuration in the present study. b) By the usage of local top-gates it is possible both at 4.2 K and 300 K to deplete the conducting regions below the gates and subsequently continuously reduce the width of the remaining conducting channel between the gates. The figure is taken from reference [51].

However, issues with top-gating often can arise due to electrical breakdown through defects in the gate dielectric whereupon leakage currents shunt the gate and interface electronic system. This shunting prevents further tuning of the interface charge carrier density and other physical properties. Consequently, another top-gating method have widely been employed for STO-based heterostructures where an ideally insulating gate composed of ionic liquid is dispensed on top of the oxide heterostructure (see Figure 2-1d). While in its liquid state, the ionic species in the dispensed gate are free to rearrange and segregate into an effective dipole layer, which exerts a substantial electric field on the STO-based heterointerface below. Upon cooling of the sample, the ionic species are frozen into place and thus prevent current flow to occur while still maintaining the imposed large electric field. Ionic liquid gating of LAO/STO using this electrical double layer approach was studied by Zeng et al. where a modulation of the charge carrier density was observed to be possible up to \( 3.0 \times 10^{13} \text{ cm}^{-2} \) at 2-3 K (see Figure 2-6)[26]. In other studies, the induced carrier density was found to be 1-2 orders of magnitude larger[56,57].

![Figure 2-6](image)

**Figure 2-6** a) Schematic illustration of the gating configuration in the present study. b) The ionic liquid gating allows a large tuning of the charge carrier density in LAO/STO heterostructures at 2-3 K, however, with a need to exceed the freezing point of the liquid between each gate voltage applied for thawing the ionic liquid. The figure is taken from reference [26].

By combining this ionic liquid setup with a back-gate in a dual-electrostatic configuration, it was shown possible by Lin et al. to obtain a larger modulation of the charge carrier density between \( 5.0 \times 10^{12} \) and \( 5.0 \times 10^{13} \text{ cm}^{-2} \) at 180 K (see Figure 2-7)[26].

![Figure 2-7](image)

**Figure 2-7** a) Schematic illustration of the gating configuration in the present study. b) The combined usage of a back-gate and ionic liquid allows charge carrier density changes approaching one order of magnitude at 180 K. The figure is taken from reference [58].
By scanning a positively charged tip of a conducting atomic force microscope (c-AFM, see Figure 2-1e) at room temperature across the surface of heterostructures just below the metal/insulator transition (with 3 u.c. LAO grown on STO), the surface can be protonated and locally induce a metastable interface conductivity\cite{27,59}. Vice versa, passing a negatively charged c-AFM tip will remove this metastable interface conductivity. In this way, one can write and erase conducting channels at the LAO/STO interface with nanoscale lateral dimensions. This metastable gating method (also known as charge writing), have led to remarkable discoveries stemming from the behavior of correlated electrons e.g. electron pairing without superconductivity\cite{50} and testifies to the rich phase diagram of STO. Concerning charge carrier modulation by gating, it was early demonstrated by Cen et al. that the written conducting channels likewise can act as gate-electrodes themselves with lateral transistor behavior possible at low temperatures (see Figure 2-8)\cite{28}.

Figure 2-8 a) Schematic illustration of the gating configuration in the present study. b) Using the positively charged tip of a c-AFM, it is possible at 300 K to induce metastable conducting paths in the nominally insulating LAO/STO heterostructures. c,d) These written nanocircuits can themselves act as lateral gates displaying field effect transistor behavior at 2 K as measured by the current/voltage characteristics between the source and drain (I_D vs V_SD) upon application of different gate voltages (V_GD). The figure is taken from reference \cite{28}.

We have so far only described STO-based heterointerfaces where the charge carriers are electrons. However, following the thin film stacking sequence previously investigated\cite{60}, the STO/LAO/STO heterostructure was proven to exhibit a two-dimensional hole gas by Lee et al.\cite{61}. Here, the top STO/LAO interface hosts a hole gas whereas the bottom LAO/STO interface simultaneously hosts an
electron gas. The low temperature back-gating of this dual electron-hole system was soon after studied by Singh et al. (see Figure 2-9)\cite{62}. For this parallel plate capacitor system with three capacitor plates composed of the back-gate, electron gas and hole gas, the authors found an increase of both the electrons and holes when applying a larger positive voltage on the back-gate.

![Figure 2-9](image1)

**Figure 2-9** a) Schematic illustration of the gating configuration in the present study. b) The dual electron-hole system in STO/LAO/STO heterostructures can readily be gated at 2 K by the electric field from a back-gate with largest modulation of the hole density. c) Back-gating at 2 K of the ordinary two-dimensional electron gas in LAO/STO heterostructures show similar characteristics as previously observed for this system. The figure is taken from reference \cite{62}.

b) **Gating of electron mobility:**

Modulations of the charge carrier mobility can likewise be induced using gating. When the quantum well in STO is subjected to the application of an external electric field, aside from changing the occupation of the well, the confining potential changes as well. This change can consequently affect the average scattering time of electrons, which in turn can alter their corresponding carrier mobility value. By gating through the STO substrate with a back-gate, it was found by Bell et al. that this modulation can induce much larger changes in the electron mobility than carrier density at 2 K (see Figure 2-10)\cite{63}. Moreover, the dependence of electron mobility with back-gate voltage was found to correlate positively with the carrier density modulation, i.e. with positive voltages applied resulting in larger electron mobilities as well as more charge carriers and vice versa. It is worth noting that this trend is opposite to the typical reciprocal relationship between electron mobility and charge carrier density in as-grown STO-based heterointerfaces\cite{64,65}, which may be explained by a stronger scattering at the interface due e.g. broken lattice symmetry, STO vicinal steps or preferential defect formation at the interface\cite{66,67}.

![Figure 2-10](image2)

**Figure 2-10** a) Schematic illustration of the gating configuration in the present study. b) Here, the authors found a primary modulation of the electron mobility over the carrier density when the electric field was applied from a back-gate at 2 K. The carrier density and mobility are extracted using the Hall coefficient at 2 and 8 T. The heavy lines are changes in the carrier density expected from the capacitance. The figure is taken from reference \cite{63}.

Smink et al. studied the effect on low-temperature electron mobility in different bands by top-gating of STO/SrCuO$_2$/LAO/STO (see Figure 2-11)\cite{46}. In this study the authors found that although the overall mobility is reduced upon increasing the applied voltage from the top-gate, the electron mobility of the individual sub-bands is expected to change much less as the band occupation is varied.
Applying electrostatic gating by an ionic liquid was, on the other hand, demonstrated by Zeng et al. and it was found to have a profound effect on the low-temperature electron mobility in LAO/STO heterostructures (see Figure 2-12) leading to electron mobilities approaching 20,000 cm^2/Vs. This high mobility allowed the observation of Shubnikov-de Haas oscillations (see later in this section and Section 3).

The low temperature back-gate dependence of carrier mobility in the previously mentioned dual electron-hole system in STO/LAO/STO heterostructures was also investigated by Singh et al. (see Figure 2-13). The authors of this study elucidated that while electrons behave similar to when being hosted at the simple electron gas LAO/STO heterointerface, holes might display a non-monotonic dependence with back-gate voltage assuming a maximal value for certain gate voltages. This trend, however, needs to be further investigated by sampling with finer resolved gate-voltage values.

c) Gating of superconductivity:
A unique property of STO-based heterostructures is the gate tunability of the superconducting phase. Superconductivity in bulk STO appears at very low carrier concentrations making it the most dilute superconductor found in nature. Interestingly, because of its peculiar dome-shaped phase diagram for superconductivity, STO partly motivated the search for high-temperature superconductors. The critical transition temperature for STO shows a dome-shaped dependence on the carrier density with a maximum value of \( T_c \approx 400 \text{ mK} \) for \( n \sim 10^{20} \text{ cm}^{-3} \). The dome-shaped dependence of \( T_c \) as well as the emergence of superconductivity at low carrier densities allow for inducing a normal conductor-superconductor phase transition at a fixed temperature using gating.

Figure 2-11 a) Schematic illustration of the gating configuration in the present study. b) Electron mobility of the individual sub-bands in STO/SrCuO_2/LAO/STO as a function of the top-gate potential. The figure is taken from reference [46].

Figure 2-12 a) Schematic illustration of the gating configuration in the present study. b) While gating with ionic liquid at 2-3 K it is possible to enhance the electron mobility up to values approaching 20,000 cm^2/Vs. The figure is taken from reference [26].

Figure 2-13 a) Schematic illustration of the gating configuration in the present study. b) The hole and electron mobility in STO/LAO/STO heterostructures appears to respond unequally to the influence of electric field from a back-gate at 2 K with the hole mobility seemingly displaying a maximal value at a certain critical gate voltage. c) The electron mobility of individual sub-bands in LAO/STO heterostructures show similar response to back-gate voltage at 2 K as previously observed for this system. The figure is taken from reference [62].
After the discovery of interface superconductivity in STO-based heterostructures\(^7\), its back-gating behavior was studied by Caviglia et al. where a dome-shaped dependence with carrier density was also found (see Figure 2-14\(^7\)). Subsequently, several groups have found a similar behavior of the superconducting phase in other STO-based heterostructures, e.g. amorphous-LAO/STO\(^7\). On the other hand, Lin et al. argued by considering the bulk SrTiO\(_3\) that the interface and bulk superconducting phases are behaving differently\(^7\).

**Figure 2-14** a) Schematic illustration of the gating configuration in the present study. b) The superconducting transition of LAO/STO heterointerfaces can be tuned by the back-gate potential \((V_g)\) with the critical transition temperature \((T_{K}\)) tunable from 300 mK and below. The figure is taken from reference \(^7\).

In order to investigate the origin of the superconducting phase, multiple groups have used electrostatic gating as a handle to aid in its understanding. Singh et al. for instance concluded based on resonant microwave transport and back-gating experiments that the emergence of superconductivity was linked to the carrier population of higher energy \(d_{xz}\) subbands in STO (see Figure 2-15\(^7\)). This indicates that the system transitions from initially being an array of weakly coupled Josephson junctions to a homogenous superconductor as the carrier density is increased by back-gating. Thus, the maximal critical temperature is expected to occur above the Lifshitz transition in the phase diagram where \(d_{xz}\) subbands start to become populated. The authors ascribe this maximal critical temperature to a competition between electron pairing and phase coherence.

**Figure 2-15** a) Schematic illustration of the gating configuration in the present study. b) Sub-band carrier densities extracted from two-band fits as a function of top-gate potential \((V_G)\) mapped with the superconducting phase. c) Superfluid density \((n_{s2D})\) calculated from superconducting critical current compared with carrier density of the high effective mass sub-band \((d_{xz}/d_{yz})\). The figure is taken from reference \(^7\).

Ultimately the relationship between the emergence of superconductivity and carrier density as well as electron mobility is still not fully understood. As the gate modulation is expected to change the quantum well confinement and the effective carrier density, it is consequently difficult to disentangle the effects of gate-tuned carrier densities and electron mobility on superconductivity. To this vein, Smink et al. studied the effects of performing top- and back-gating (separately or simultaneously) in LAO/STO heterostructures on superconductivity (see Figure 2-16\(^7\)). In this study, the authors found that the electrostatic effects on the critical temperature with electric fields applied from top- and back-gates where not identical. Thus, by studying the combined effects of applying top- and back-gate voltages simultaneously and independently, it was shown possible to carefully tune the emergence of the superconducting phase. The authors ascribed the maximal critical temperature to occur when the second \(d_{xy}\) sub-band becomes depleted above the Lifshitz transition. Here, it is worth recalling from subsection 2a that the carrier density of \(d_{xy}\) subbands was found to be reduced above the Lifshitz transition.
Finally, a number of studies have investigated the effects of laterally constricting the superconductivity by top-gating. For instance, it was demonstrated by Monteiro et al. that the aforementioned Josephson junctions can be formed at STO-based heterointerfaces (see Figure 2-17)[52]. Fluctuations of the critical current through a single Josephson junction was demonstrated in this study. Moreover, the gate-tunable Josephson junction was shown to display superconducting quantum interference oscillations of the critical current through the junction as a function of the externally applied magnetic field.

**Figure 2-17** a) Schematic illustration of the gating configuration in the present study. b,c) The local side-gates allow a constriction of the superconducting phase whereupon fluctuations of the critical current consequently appear. These fluctuations are reminiscent of charge tunneling through a single Josephson junction. The figure is taken from reference [52].

d) Gating of spin-orbit coupling:
One of the defining features of charge carriers residing at STO-based heterointerfaces, is a significant gate-tunable Rashba spin-orbit coupling. In the pioneering works of Caviglia et al. and Ben Shalom et al. the low-temperature spin-orbit coupling of LAO/STO was studied from two different angles: magnetotransport and superconductivity (see Figure 2-18)[77,78]. In both of these works it was inferred that it is possible to tune the spin-orbit coupling by an order of magnitude in the investigated range of back-gate voltages. Both studies supported a non-monotonic dependence of the spin-orbit coupling with the largest values found to coincide with maximal critical temperature for superconductivity.
However, from the back-gate geometry employed in these two studies it is not trivial to disentangle the effects of charge carrier density, electron mobility, sub-band occupation and quantum well confinement to the resulting spin-orbit coupling. As described in the previous subsections, it is clear that each of these critical parameters (responsible for the spin-orbit coupling) responds dissimilarly upon application of an electric field as well as unequally to different gating geometries. The dependence of spin-orbit coupling on applied top-gate voltage was studied by Hurand et al.\cite{79}. In this study, the Rashba spin-orbit coupling was found to linearly depend on the applied top-gate voltage, with larger spin-orbit splitting as the gate voltage was increased (See Figure 2-19). Curiously, this dependence did not show much correlation with the position of the superconducting phase as was the case in the previous two studies by Caviglia et al. and Ben Shalom et al.\cite{77,78,79}.

In a later study, Niu et al. studied the low-temperature ionic liquid gating of $\gamma$-Al$_2$O$_3$/STO (GAO/STO) where a non-monotonic dependence on the spin-orbit coupling likewise was found (see Figure 2-20)\cite{80}. This study will be revisited later in Section 3.
function of ionic liquid gate voltage. The figure is taken from reference [80].

One principal consequence of the magnitude of the spin-orbit coupling is to be able to dictate the efficiency for spin-to-charge interconversion. Spin-to-charge conversion was demonstrated in NiFe/LAO/STO by Lesne et al.\cite{81}. It was found that the electric field from a back-gate at 15 K not only controls the magnitude of generated charge current but also the sign. This sign change of the effective Rashba coefficient was explained by the two types of relevant $t_{2g}$ subbands in STO ($d_{xy}$ and $d_{xz}/d_{yz}$) having opposite Rashba coefficient signs. In this way, the relative population of each of the two types would correspond to an effective overall Rashba coefficient that in turn would dictate the net spin-to-charge conversion (see also Section 3).

e) Gating of magnetism:
Magnetic order and exchange coupling strength in STO-based heterostructures have been shown to depend on electrostatic gating. This was investigated at low temperatures using anisotropic magnetoresistance and anomalous Hall effect of back-gated LAO/STO by Joshua et al.\cite{82}. In this study, it was found that the interface system displays a large field anisotropy and spin polarization above the Lifshitz transition originating from an exchange coupling between localized $d_{xy}$ magnetic moments and the itinerant electrons. The relative carrier population of the $d_{xy}$ vs. $d_{xz}/d_{yz}$ plays a significant role in determining the resulting magnetic properties of the interface. Here, a ferromagnetic coupling between localized $d_{xy}$ magnetic moments and $d_{xz}/d_{yz}$ itinerant electrons was proposed to compete with an antiferromagnetic coupling between the magnetic moments and $d_{xy}$ itinerant electrons. The magnetic state at room temperature proposed to originate from the localized $d_{xy}$ electrons was furthermore modulated by Bi et al.\cite{83}. Using magnetic force microscopy, the authors found it possible to induce and observe in-plane ferromagnetic phases. In another seminal study of magnetic interactions at STO-based conducting interfaces, Stornaiuolo et al. studied the effect of inserting a ferromagnetic spacer layer (EuTiO$_3$) between LAO and STO\cite{84}. Below the ferromagnetic transition temperature of EuTiO$_3$, an exchange coupling was found between the localized moments of Eu atoms and the above-mentioned electrons in Ti 3$d$ orbitals. This resulting magnetic state was found to be gate tunable as observed from the anomalous Hall effect, with a sharp transition around a few tens of volts (see Figure 2-21). The co-existence of a superconducting phase was also found to be present in this heterostructure despite the presence of the EuTiO$_3$ layer.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2-21.png}
\caption{a) Schematic illustration of the gating configuration in the present study. b) The back-gate voltage dependence of the coefficient in the anomalous Hall effect ($R_{xy}^A$) at a fixed temperature of 1.8 K. c) The temperature dependence of the anomalous Hall effect gated well into the exchange coupling regime. The figure is taken from reference [84].}
\end{figure}

f) Gating of local microstructure and domain walls:
One physical property that has been shown possible to modulate is the local tetragonal microstructure and domain walls at temperatures below 105 K. A couple of studies have demonstrated that the tetragonal domains forming in STO below the cubic-to-tetragonal structural phase transition at 105 K can be controlled and indeed moved by the application of an electric field from a back-gate. By probing the electrostatic landscape of LAO/STO interface by a scanning field effect transistor, Honig et al. found lateral tetragonal domain motion with applied back-gate voltage at 2 K (see Figure 2-22)\cite{85}. At the same time Kalisky et al., who studied back-gated LAO/STO with a scanning superconducting quantum interference device (SQUID), found no discernible movement of such tetragonal domains under similar experimental conditions\cite{86}. The gate control of domain structure hence remains under-investigated and should be the subject of further investigations.
Figure 2-22 a) Schematic illustration of the gating configuration in the present study. b) Horizontal displacement of blue and red features corresponding to the lateral motion of tetragonal domains in LAO/STO is demonstrated to be possible with the application of an electric field from a back-gate at low-temperatures. The figure is taken from reference [85].

Gating of quantum transport phenomena:
The ability to gate the electron mobility in STO-based heterostructures opens up for the observation of quantum transport phenomena that require long mean free paths to be detectable. For example, using back-gate stimulation of delta-doped STO and La$_{7/8}$Sr$_{1/8}$MnO$_3$ buffered STO-heterointerfaces, the quantum Hall effect has been demonstrated for the first time in complex oxides [85-89]. The manifestation of the quantum Hall effect in these two systems will be covered later in Section 3. Likewise, gating by back-gate and ionic liquid have allowed observation of Shubnikov-de Haas oscillations in LAO/STO [26,90,91]. Moreover, tuning of the spin-orbit coupling and the superconducting phase have allowed the observation of electron pairing behavior without the presence of superconductivity [50,54]. Finally, by lateral gating with c-AFM written conducting paths in LAO/STO, ballistic transport of single electrons as well as electron pairs across length scales approaching 20 µm have been demonstrated [92].

2.3. Future prospects of electrostatic gating
STO possesses an incredible landscape of physical properties that can be electrostatically modulated simultaneously by application of the electric field from a gate. Due to this intertwined nature of the physical properties, the key to unlocking the future potential of STO-based devices with novel functionalities may lie in disentangling the degrees of freedom, e.g. by double gating, applications of magnetic fields, structural confinement in nanowires or even quantum dots just to name a few. For example, a study by Chen *et al.* exploited the individual control of top- and back-gating to study the superconducting phase of LAO/STO [93]. The growth of STO thin films with high mobility and crystalline quality [94] further expands the possible gating geometries as it enables the design of symmetric quantum wells gated in close proximity by heavily doped epitaxial layers. Finally, unlocking and engineering the domain walls upon electrostatic gating of STO holds the prospect of many exciting discoveries to come [95].
3. Magnetic field

In this section, we review the effect of a magnetic field on STO-based heterostructures with a focus on the magnetoresistance, Hall effect, magnetic proximity effect and spin/charge interconversion.

3.1. Magnetoresistance

Magnetoresistance is the resistivity change occurring in materials subjected to the application of a magnetic field. When applying the magnetic field perpendicular to the sample surface, a positive magnetoresistance is commonly observed, whereas magnetic fields applied parallel to the surface may lead to a negative magnetoresistance. At low temperatures quantum corrections to the conductivity such as weak localization (WL) and weak anti-localization (WAL) can occur in the low magnetic field regime while Shubnikov-de Haas oscillations can appear at high magnetic fields.

a) Classical magnetoresistance

Electrons moving in a perpendicular magnetic field will deflect from their original trajectory due to the Lorentz force, leading to a positive magnetoresistance (MR) as shown in Figure 3-1a. Such a positive ordinary magnetoresistance can be observed in all metals. In a metallic system with carriers occupying only a single band, the ordinary magnetoresistance shows a parabolic field dependence due to the Lorenz force, leading to a magnetoresistance is commonly observed, whereas magnetic fields applied parallel to the surface may lead to a negative magnetoresistance. At low temperatures quantum corrections to the conductivity such as weak localization (WL) and weak anti-localization (WAL) can occur in the low magnetic field regime while Shubnikov-de Haas oscillations can appear at high magnetic fields.

b) Weak anti-localization and weak localization

Disorder at the interface becomes very important at low temperatures and may originate from various sources such as oxygen/cation vacancies, cation intermixing and tetragonal domain walls. Disorder can modify the wave behavior of electrons from extended states to localized ones, resulting in a peak in the magnetoresistance at low magnetic fields. The peak is a signature of weak localization, which originates from the path of an electron undergoing several elastic scattering events which may interfere positively with the same path traveled in the opposite direction[103]. This increases the probability of localization and hence increases the resistance. Breaking of the inversion symmetry at the interface may lead to the Rashba spin-orbit coupling, which can result in the negative interference that characterizes the weak anti-localization and produces a lowering of the resistance.[104] When magnetic fields are applied, both the positive and negative interferences are destroyed by the extra phase picked up by the Aharonov-Bohm effect. This results in a peak (dip) in the magnetoresistance around $B = 0$ T for weak localization (anti-localization).

Weak localization and anti-localization have frequently been observed in STO and STO-based heterostructures as also reviewed in Ref. [104]. The weak anti-localization provides a convenient handle to study the spin-orbit coupling, which has been shown to be tunable using electrostatic gating[77,80], as discussed in the previous section 2. This is well in line with first principles density functional theory calculations that have predicted that the Rashba spin-orbit coupling reaches a maximum due to the band hybridization at the critical point where $d_{xy}$ and $d_{xz}/d_{yz}$ bands cross.[105–107].

c) Shubnikov-de Haas oscillations

Shubnikov-de Haas oscillations are formed due to a magnetic field-induced change in the band structure and provide an accessible avenue to probe the Fermi surface at the conducting interfaces. Superimposed on the magnetoresistance background, Shubnikov-de Haas oscillations can be observed in samples with high mobility ($\geq 2000$ cm$^2$V$^{-1}$s$^{-1}$) at low temperatures ($< 5$ K) and high magnetic fields (a few T), where the requirements of $\omega_c\tau > 1$, $\hbar\omega_c > k_B T$ are fulfilled.[90] Here, $\omega_c$ and $\tau$ are the cyclotron frequency and scattering time, respectively. Many methods have been employed to achieve a high mobility in oxides as reviewed in Ref. [65]. For example, using surface treatments, Xie et al. achieved a mobility higher than 20,000 cm$^2$V$^{-1}$s$^{-1}$ for the LAO/STO system.[109] Huijben et al. incorporated a thin layer of SrCuO$_2$ between the surface of a LAO/STO heterostructure and a capping layer of STO. This enhanced the oxygen exchange and a mobility up to about 50,000 cm$^2$V$^{-1}$s$^{-1}$ was achieved due to a reduction of interfacial impurity.
scattering from oxygen vacancies\cite{47}. Chen et al. found a very high mobility of ~140,000 cm$^2$V$^{-1}$s$^{-1}$ at the spinel/perovskite heterointerface of GAO/STO.\cite{110} Shubnikov-de Haas oscillations were apparent in these high-mobility 2DEG systems, as shown in Figure 3-2a for the case of GAO/STO.

Information about the Fermi surface, carrier density, effective mass and mobility can be deduced from Shubnikov-de Haas oscillations. The angular dependence of Shubnikov-de Haas oscillations also gives information on the confinement of the heterointerfacial conducting sub-bands. This is the case since only the out-of-plane component of the magnetic field leads to Shubnikov-de Haas oscillations for the confined electrons. After optimizing the growth conditions of LAO/STO to achieve a mobility of 6600 cm$^2$V$^{-1}$s$^{-1}$, Caviglia et al. observed that the frequency of the Shubnikov-de Haas oscillations only depended on the perpendicular magnetic field component, which is consistent with two-dimensional confinement of the electron gas at the interface (see Figure 3-2b)\cite{90}.

A common observation in all the studies of Shubnikov-de Haas oscillations at STO-based heterostructures is that the carrier density deduced from the oscillation frequency ($n_{SdH}$) consistently was found smaller than the one obtained from the Hall measurements ($n_{Hall}$).\cite{108,111,112} Some mechanisms have been proposed to account for this apparent disagreement. A portion of the carriers measured using the Hall effect may suffer from extensive scattering leading to a mobility that is too low to meet the condition needed for observing Shubnikov-de Haas oscillations.\cite{113} Another possible explanation for the discrepancy relies on nontrivial degeneracies in oxide 2DEG systems. For example, the spin, valley and magnetic breakdown or orbits may lead to 2-fold, 3-fold and 4-fold degeneracies, respectively.\cite{111,114} In addition, the presence of multiple sub-bands with different carrier densities in the quantum well may also account for the difference between $n_{Hall}$ and $n_{SdH}$.\cite{87,114} The presence of complicated degeneracy or sub-bands makes it difficult to derive the accurate carrier density from Shubnikov-de Haas oscillations.

### 3.2. Hall Effect

When applying a magnetic field perpendicular to the heterointerface, different contributions to the measured Hall effect can occur such as the normal Hall effect, anomalous Hall effect\cite{115-117}, quantum Hall effect\cite{87,89,114} and spin Hall effect\cite{118}. The following gives a short description of the different types of Hall effects that have been observed in STO-based heterointerfaces.

#### a) Normal Hall effect

In a simple conductor with the conductivity occurring in a single band, the Hall resistance ($R_{xy}$) varies linearly with magnetic field. For STO-based heterostructures, the Hall resistance typically deviates from linearity at temperatures below 105 K. This deviation arises from the two sub-band occupation of the $t_{2g}$ orbitals. By carrier depletion under the application of an electric field from a gate (see Section 2), the Hall resistance can revert between non-linear and linear (see Figure 3.3) upon crossing the Lifshitz transition determining if the conducting electrons occupy a single sub-band ($d_{xy}$) or two types of subbands ($d_{xy}$ and $d_{xz}/d_{yz}$)\cite{43}.

#### b) Anomalous Hall effect

The anomalous Hall effect arises from a coupling between the itinerant electrons and magnetic moments, as observed in several oxide heterostructures\cite{82,96,100,116}. As shown in Figure 3-4a, a signature of the anomalous Hall effect is a downward curvature that bends the curve clockwise, in contrast to the aforementioned counter-clockwise bending with the non-linear Hall effect stemming from conduction in two $n$-type sub-bands. Subtracting the contribution of the ordinary Hall effect determined from the low-field slope of $R_{xy}$ vs $B$ makes the anomalous Hall effect clearer, as
displayed in Figure 3-4b. In contrast to the case in Figure 3-4, the anomalous Hall effect typically only gives a small contribution to the total Hall effect due to the weak magnetization and/or a weak coupling between itinerant moments and the magnetization. In these cases, the anomalous Hall effect can be hard to deduce directly from the raw data, whereas \( \frac{dR_{xy}}{dB} \) provides a better way of identifying this contribution. In order to make the effects of the magnetic state more pronounced, one of the common strategies used is to introduce ferromagnetism in LAO/STO using the magnetic proximity effect from magnetic dopants as discussed in Section 3.3.

![Figure 3-4](image)

**Figure 3-4** Anomalous Hall effect at the interface of GAO/STO. a) Hall resistance under various temperatures. b) Anomalous Hall effect revealed after subtracting the ordinary Hall effect. c) The component of the magnetization perpendicular to the interface. The figure is taken from Ref. [100].

c) Quantum Hall effect

By improving the electron mobility of the 2DEG in STO-based heterostructures, observation of the quantum Hall effect is possible. This has been observed in the modulation-doped amorphous-LAO/STO heterostructure, which exhibits both high electron mobility exceeding 10,000 cm²V⁻¹s⁻¹ and low carrier density on the order of \( \sim 10^{12} \) cm⁻² at temperatures below 1 K. As shown in Figure 3-5a, the magnetic field dependence of \( R_{xx} \) shows quantum oscillations at a temperature of 30 mK and a gate voltage of 6 V. Concomitantly, \( R_{xy} \) exhibits a step-like behavior as a function of \( B \) where the minima in \( dR_{xy}/dB \) coincide with the minima in \( R_{xx} \). Surprisingly, \( R_{xy}^{-1} \) does not show steps with integer values of \( e^2/h \) as always observed in conventional semiconductor quantum wells comprised of a single band. Moreover, as shown in Figure 3-5b, the value of \( R_{xy}^{-1} \) for the same plateau varies as a function of \( V_G \) in contrast to the case of conventional semiconductors where it remains constant. The plateaus, however, appear regularly spaced for all \( V_G \) with either \( \Delta R_{xy}^{-1} \sim 10 \pm 2 \frac{e^2}{h} \) or \( \Delta R_{xy}^{-1} \sim 20 \pm 2 \frac{e^2}{h} \) for \( B > 6 \) T and \( B < 6 \) T, respectively. Trier et al. conclude that when the carrier density is below the Lifshitz point, the interface 2DEG is comprised of a single quantum well with multiple parallel conducting channels, here 10, as displayed in Figure 3-5c. These channels have a similar effective mass and Hall mobility, whereas their individual carrier densities differ. While the mean carrier density approximately was concluded to dictate the frequency of Shubnikov-de Haas oscillations, the total carrier density from these channels correspond to that measured from the Hall effect \( n_{Hall} \). This provided a possible explanation for the commonly observed difference between \( n_{Hall} \) and \( n_{SdH} \).
d) Spin Hall effect

In a system with a strong spin-orbit interaction, a longitudinal charge current can give rise to transverse spin current via the spin Hall effect. Jin et al. demonstrated a sizeable spin/charge interconversion through the spin Hall effect in LAO/STO. As shown in Figure 3-6a, an injected charge current through two opposing Hall bar probes can, via the direct spin Hall effect, induce a transverse spin current. If the polarization of the spins is not lost before they reach a neighboring probe pair, the spins can become reconverted into a charge current through the inverse spin Hall effect and induce a detectable nonlocal voltage. The spin diffusion induced by the spin Hall effect through the bridging channel in the Hall bar device can be confirmed by the signature of spin precession and the dependence on probe spacing. The nonlocal voltage as a function of in-plane magnetic field produced a Hanle curve as shown in Figure 3-6b. Here, the spin Hall effect induces the spin current along the bridging channel with its polarization perpendicular to the plane. Thus, the in-plane magnetic field causes the Larmor precession of spins. The Hanle curves shown in Figure 3-6b displayed a narrower width for the longer channel because the transit time for the carrier spin to process was increased. The amplitude of the non-local resistance signal was also shown to decay exponentially with the channel length (see Figure 3-6c).

3.3. Magnetic Proximity Effect

The possible two-dimensional magnetic ground state at LAO/STO have attracted great interest, although it remains elusive whether the ground state of the LAO/STO system is ferromagnetic. One of the common strategies to introduce ferromagnetism in LAO/STO is through the magnetic proximity effect where magnetic dopants are used to induce or enhance the magnetic state in their vicinity. Anomalous Hall effect provides strong evidence of coupling between itinerant electrons and magnetic moments, as shown in Figure 3-7. As also described in Section 2, Stornaiuolo et al. reported a gate-controlled spin-polarized 2DEG by inserting a few unit cells of ferromagnetic EuTiO$_3$ at the LAO/STO interface. In this system, the exchange interaction between the magnetic moments of Eu-4$f$ and Ti-3$d$ electrons is dominant. Zhang et al. observed a similar anomalous Hall effect at a La$_{7/8}$Sr$_{1/8}$MnO$_3$-
buffered LAO/STO interface. In this case, Mn ions provide a magnetic scattering center with the local magnetic moment on Mn$^{2+}$ or Mn$^{3+}$. However, these spin-polarized electrons have been detected often in the high carrier density range where both the $d_{xy}$ and $d_{xz}/d_{yz}$ electrons are populated.\[119\] Based on the ferromagnetism of LMO thin films on the STO,\[120\] Gan et al. later detected the anomalous Hall effect in oxide interfaces of LaAl$_0.7$Mn$_0.3$O$_3$/STO where only the $d_{xy}$ band is populated.\[96\]

Since superconductivity has been reported widely at the LAO/STO interface (see Section 2), the magnetic proximity effect not only provides an effective way to induce/create ferromagnetic states, but also opens a door to explore the coexistence of superconductivity and magnetism. In a conventional physical picture, superconductivity and ferromagnetism are mutually exclusive phenomena, but a possible coexistence has been reported both in Stornaiuolo’s and Gan’s studies\[84,96\] as well as in regular LAO/STO heterostructures without magnetic proximity effects\[121,122\]. The former study suggested that the ferromagnetism and superconductivity possibly occur in different bands that are spatially separated from each other. However, this suggestion was challenged by Gan et al. who observed the spin-polarized and superconductive $d_{xy}$ electrons in a single device with only $d_{xy}$ subbands occupied.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure3-7.png}
\caption{Magnetic proximity effect in LAO/STO systems. a) A negative curvature at low field suggestive of the anomalous Hall effect has been observed in LAO/EuTiO$_3$/STO heterostructure for $V_g > -30$ V. b) The anomalous Hall effect observed at LAO/La$_{2/3}$Sr$_{1/3}$MnO$_3$(1 nm)/STO interfaces and its deduced anomalous Hall resistance as a function of gate voltage. c) The anomalous Hall effect detected at LaAl$_0.7$Mn$_0.3$O$_3$/STO interfaces. The figures are taken from Ref. \[84\], \[119\] and \[96\].}
\end{figure}

### 3.4. Spin/charge interconversion

The giant tunable Rashba spin-orbit coupling, high mobility and long momentum relaxation time at the oxide interfaces provide a promising combination for applications in spintronics.\[123-125\] Using a three-terminal device, Reyren et al. first reported injection of a spin current from a ferromagnetic Co layer into the LAO/STO 2DEG through Hanle experiments. They attributed this injection to take place through defects in LAO.\[126\] However, Swartz et al. argued that the signal measured by the three-terminal geometry should be attributed to spurious effects such as spin traps rather than the spin accumulation.\[112\] The four-terminal non-local configuration gives opportunities for interpreting the spin-related effects unambiguously, as displayed in Figure 3-8a.

Besides transport experiments, spin pumping from ferromagnetic resonance experiments provides an effective avenue to inject spin currents (Figure 3-8b). In two-dimensional systems, Rashba spin-orbit coupling induced by inversion symmetry breaking allows the charge-spin interconversion by direct and inverse Edelstein effect. Lesne et al. injected a spin current from permalloy into the 2DEG at the interface of LAO/STO by performing spin pumping ferromagnetic resonance experiments. Herein, a 3D spin current was converted into 2D charge current due to the inverse Edelstein effect and the spin-to-charge conversion efficiency was unprecedented high with $\lambda_{\text{IEE}} = 6.4$ nm at $T = 7$ K where the inverse Edelstein effect length, $\lambda_{\text{IEE}}$, indicates the efficiency of spin-to-charge conversion.\[81\] Using the same method, Chauleau et al. achieved temperature-dependent spin-to-charge conversion, the $\lambda_{\text{IEE}}$ was 1 nm at 77 K and decreased upon increasing temperature.\[129\]. Beyond the scope of LAO/STO, Zhang et al. injected a spin current into the conducting STO surface, but the spin-to-charge efficiency was low with $\lambda_{\text{IEE}} = 0.23$ nm at room temperature, which might be due to the surface roughness of Ar$^+$ irradiated STO samples.\[130\] Later, Han et al. achieved successful spin-to-charge conversion in LAO/STO 2DEG systems with different LAO thickness ranging from 3 to 40 u.c. There is a striking discrepancy between their results and previous reports as high efficiency spin-to-charge conversion only occurred at room temperature in their samples. Surprisingly, when the thickness of LAO reached 40 u.c., spin current was still injected into 2DEG at the interface.\[131\] This indicates that spin current transport in LAO occurs via a mechanism\[126\], such as defect hopping, which requires further exploring. It is proposed that the giant Rashba spin splitting at STO surface\[132\], and at the interface of GAO/STO with extremely high mobility\[110\] could yield a new record of conversion efficiency with a value of $\lambda_{\text{IEE}}$ beyond 100 nm.\[124\] Moreover, the tunability of the Rashba spin-orbit coupling via electrostatic gating opens new pathways for manipulating the spin-to-charge conversion process. Lesne et al. and Han et al. had already enhanced and controlled the conversion efficiency by applying gate bias.\[81,128\]
Spin-orbit coupling related spin-orbit torque can affect the magnetization effectively, showing potential in low power consumption, high density and fast speed magnetic random access memories. Highly efficient charge-to-spin conversion is the key factor for the spin-orbit torque technique. Direct charge-to-spin conversion via the Edelstein effect remains scarce. Charge-to-spin conversion in oxide interface was firstly demonstrated by Wang et al. via spin torque ferromagnetic resonance (Figure 3-8c). The conversion efficiency was estimated to be 6.3 and inelastic tunneling via localized states in LAO was attributed to the spin transmission process.\[128\]

3.5. Perspective
The interfaces of transition metal oxides exhibit a tunable spin-orbit coupling, which may find use within quantum computations and multifunctional spintronic devices\[133\]. STO-based 2DEG systems can achieve gate-tunable spin-to-charge interconversion with a high efficiency as well as being a good spin conductor with long-range spin transport. Prediction for STO with its large Rashba splitting and for the interface of GAO/STO with the high mobility suggests that a new record for the spin-to-charge conversion, $\lambda_{\text{IEE}}$ exceeding 100 nm could be achieved, which exceeds that of LAO/STO by an order of magnitude.\[124\] Since the performance of spintronic device is limited by the efficiency of spin-charge interconversion, pursuing the high efficiency in these two STO-based systems is of great significance and value. However, this efficiency may be highly reduced by the capping layer such as LAO and GAO, which impede the spin transferred from the magnetic layer to the interface. The mechanism for the transmission of the spin current to the interface is still unclear and needs further investigations. More efforts should be given to the parasitic effects and spurious signals from the spin pumping of NiFe ferromagnetic layer. A spin current was injected into ferromagnetic 2DEG via spin Seebeck effect in the system of EuO/KTaO$_3$\[134\], providing an inspiration for an effective pathway for the spin-to-charge conversion.
4. Light/matter interaction

Among the large spectrum of attractive properties and emergent phenomena at oxide heterointerfaces, some of the most fascinating properties are found upon light illumination. Light illumination can generate electron-hole pairs, which not only can contribute to the conductivity but also affect the diffusion of oxygen vacancies and thereby significantly modify the transport properties. For example, tunable persistent photocconductivity has been reported in STO-based heterointerfaces and combining light illumination with a gate bias, an enhancement of the resistance gatability has been demonstrated. In this section, we review the optical tunability and the underlying physical mechanisms. The application of light may offer new insights toward all-oxide optoelectronics devices.

4.1. Persistent Photoconductivity

Persistent photocconductivity (PPC) is an effect where the conductivity is increased upon light illumination and remains increased after the light is turned off. This enhanced conductivity may persist for days after turning off the light, which offers new opportunity toward the photoelectronic applications, such as radiation detectors. In conventional semiconductors, such as AlGaAs/GaN or Si membranes, PPC has already been reported. However, their practical application is limited by the low magnitude of the PPC or the low operation temperature. A large PPC was observed at room temperature in the LAO/STO heterostructure, when illuminated either by a UV lamp of 395 nm or with visible light, as shown in Figure 4-1. The photo-induced conductance is increased by 5 orders of magnitude, much higher than the one observed in conventional semiconductor heterostructures. Generally, the PPC is attributed to a spatial separation of the photoexcited electron-hole pair in LAO/STO heterostructures. Due to the existence of this induced photoconductivity, special care should be taken before performing transport measurements, such as storing the sample in dark for more than 24 hours.

![Figure 4-1. Normalized photo-induced conductance at STO or the interface of LAO/STO kept in dark or illuminated with a 395 nm UV lamp (pink dots) or visible light (blue dots). The figure is taken from Ref.](image)

Similar illumination experiments were carried out by Guduru et al. at the LAO/STO interface with a LAO layer thickness of 10 nm, as shown in Figure 4-2a. Here, they illuminated the interface with different photon energies ranging from 1.44 to 3.65 eV. Upon illumination, the resistance decreased gradually with increasing photon energy, however, with a relatively small decrease observed when the photon energy was smaller than the band gap of STO at approximately 3.4 eV. The authors attributed these small changes to the reduced absorption of light by in-gap states in STO. However, when the photon energy exceeded the band gap, the PPC was enhanced by more than 50%. Using Hall measurements without or with light, the authors found a transition from a linear Hall resistance to a nonlinear Hall resistance (Figure 4-3 b). This suggests that additional parallel conducting channel was created by the illumination.

![Figure 4-2. a) Resistance as a function of time during the illumination with different photon energies. b) Hall resistance without or with illumination by a photon energy of 3.65 eV at 4.2 K. The figure is taken from Ref.](image)

4.2. Modulation of the PPC Effect

The conductivity, carrier density, mobility and even the electronic structure of STO-based heterointerfaces are found to be very sensitive to the growth condition and in particular to the oxygen pressure and the growth temperature. Likewise, the magnitude and relaxation dynamics of the PPC effect also depend crucially on the growth parameters, doping and surface treatment as will be discussed in the following.

a) The effects of doping

Tailoring the properties of heterointerfaces, such as the ground state and metal-insulator transitions, remains challenging, but substitution or doping may provide an effective way of tuning oxide interfaces. In conventional semiconductors, such as GaAs, a large enhancement is achieved in the relaxation process of the PPC effect by Cr doping. Motivated by this, Dogra et al. substituted Al with Cr during growth of LAO in LAO/STO heterostructures. Here, electron correlations are expected to be increased due to the 3d character of Cr which led to an enhanced photo-response and decay time. In addition, Rastogi et al. have investigated the effect of δ-doping on the change in the photococonductivity in the LAO/STO interface using an insulating LaMnO3 monolayer. The authors found that photo-response of the δ-doped LAO/STO interface shifts towards a lower photon energy and has a large photo-response while the pristine LAO/STO heterointerface is sensitive to near-ultraviolet radiation and has a relatively small change in resistance upon illumination. Yan et al. investigated the transport properties of LaAl1-xNiO3/STO under light irradiation after substituting Al with Ni. The relative photo-induced resistance changes were improved from 800% to 6600% upon increasing the dopant level of Ni from x = 0 to 0.05. They attributed this change to the band bending and the larger ionic size of Ni compared to Al, which may cause defects that can hinder the recombination of electrons and holes.

b) The effects of surface treatment

Although the conducting interface in STO-based heterostructures is capped by an oxide thin film, the interaction with surface adsorbed species on the oxide top-layer can very heavily influence the interface 2DEG (see Section 6). In this vein, Xie et al. have...
showed that surface states can be changed by polar liquids leading to a prominent impact on the transport properties of the heterointerfaces. Brown et al. achieved a giant reversible switching of the conductivity at the interface of LAO and STO by means of immersing the sample in deionized water and exposing it to light as shown in Figure 4-3a. By applying water to the surface, the interface turned insulating. The conducting states could be recovered by illumination using a broadband light. The reversible switching induced 4 orders of magnitude change in the resistance and was attributed to the protonation and deprotonation of the LAO layer. The tuning of the interfacial conductivity was also carried out using surface absorbents by depositing Pd nanoparticles with a size of 2 nm on the surface of LAO. Compared to the bare LAO/STO and LAO/STO with Pd nanoparticles deposited on the LAO surface, the interface turned insulating. The conducting states could be recovered by illumination using a broadband light. The reversible switching induced 4 orders of magnitude change in the resistance and was attributed to the protonation and deprotonation of the LAO layer.

Tuning of the interfacial conductivity was also carried out using surface absorbents by depositing Pd nanoparticles with a size of 2 nm on the surface of LAO. Compared to the bare LAO/STO and LAO/STO with Pd nanoparticles deposited on the LAO surface, the interface turned insulating. The conducting states could be recovered by illumination using a broadband light. The reversible switching induced 4 orders of magnitude change in the resistance and was attributed to the protonation and deprotonation of the LAO layer.

Figure 4-3. a) Reversible transition between a conductive and insulating state by exposure to water and light. b) Optical switching of the LAO/STO interface resistance induced by periodic illumination of a 365 nm UV light for the cases of bare LAO/STO and LAO/STO with Pd nanoparticles deposited on the LAO surface. The figures are taken from Ref. [154] and [155].

4.3 Combined effect of gate bias and light illumination

Electrostatic gating and light illumination are two common and independent ways used to tune the carrier density, electronic structure and ground state of oxide heterointerfaces. Gate bias provides an effective way to accumulate or deplete carriers (see Section 2), while light illumination can generate extra carriers from promotion of itinerant carriers from the valence band or trapped states, for instance the in-gap states of STO. Lei et al. reported a significantly enlarged gate bias dependence when it is coupled to light illumination. As sketched in Figure 4-4a, they applied electrostatic gating and light illumination simultaneously at the epitaxial LAO/STO interface as well as the amorphous-LAO/STO interface. Without illumination, as displayed in Figure 4-4b, the authors found two responses when applying a negative bias: a slight rapid jump in resistance due to the capacitive depletion of carriers and a subsequent slow incremental increase attributed to a redistribution of oxygen vacancies. Once applying light illumination, the slow process presumably caused by of oxygen vacancies was accelerated dramatically and the interface resistance was turned “OFF” by a 200-fold increase in the resistance as seen in Figure 4-4b. The combined effect of light illumination and application of a negative bias results in a decrease in the carrier density, rather than an accumulation as expected from light illumination alone. Further investigation have revealed that this cooperative effect on the metallic heterointerface is temperature sensitive; this effect was relatively weak at the intermediate regime of temperature (50 K ≤ T ≤ 200 K) but strong at temperatures of T < 50 K and T > 200 K. In contrast to the long recovery by electrostatic gating, an instantaneous transition to the metallic ground state was achieved by the illumination with visible light as reported by Safeen et al.

Encouraged by the tunability of this joint effect where gate bias is combined with light illumination, Cheng et al. demonstrated that the quantum states could also be tuned via a gating effect by light at the STO-based interfaces, as shown in Figure 4-5. The transition from weak localization to weak anti-localization implies that the Rashba spin-orbit coupling is tunable by the light illumination with different wavelengths (470 and 940 nm). In contrast to the conventional electrostatic gating at low temperatures (see Section 2), this optical manipulation is nonvolatile and the tunability of the spin-orbit coupling persists after turning off the light. The effect of the light could, however, be removed by warming up the sample to room temperature and then cooling it down to 1.5 K. This advantage shows promising application for the optical nonvolatile devices. Zhang et al. have expanded the application of optical gating to other oxide heterointerfaces such as KTaO3-based 2DEGs. In their KTaO3-based samples, the Fermi energy was tuned from 13 meV to 488 meV via optical gating leading to a control of the electronic structure and the Lifshitz transition, which echoes previous theoretical predictions and experimental findings in STO-based 2DEGs.
photodoping with different wavelength (470 nm and 940 nm). For each wavelength, the LAO/STO sample has been subjected to one illumination step followed by a measurement of the magnetococonductance (∆σ). This has been repeated, giving rise to different curves with the darkest blue being the initial curve and the darkest red being the curve after around 25 times illumination. The figure is taken from Ref. [139].

4.4 Other phenomena induced by light illumination

a) Suppression of Kondo effect

A resistance upturn for T < 20 K is often observed in STO-based systems and it is frequently attributed to the Kondo effect. The Kondo effect arises as the itinerant electrons interact with the magnetic moments, such as localized carriers associated with oxygen vacancies.[58,80,161] Jin et al. first reported that the Kondo effect at the LAO/STO interface could be suppressed under the illumination of ultraviolet light.[162] Later, in LaAl1-xNiO3/STO, it was found that the Kondo effect could be enhanced by increasing the Ni level from x = 0 to 0.05 as the dopants provided localized spin centers, but after light irradiation this effect was also reduced.[151] Similarly, the Kondo effect was also found to be suppressed under the visible light of 650 nm in amorphous-LAO/STO.[163] It was proposed that the coherence between the localized spin centers was minimized by the light irradiation thus suppressing the Kondo effect. Concomitant with this suppression of the Kondo effect by light illumination, the mobility at the interface was enhanced from ~ 50 cm²V⁻¹s⁻¹ without light irradiation to 125 cm²V⁻¹s⁻¹ while the carrier density was unchanged at a temperature of 2 K.[163]

b) Photon-induced oxygen vacancies

In contrast to using the light illumination to probe the interface properties, additional effects such as formation of oxygen vacancies is often experienced when irradiating with synchrotron radiation.[164–167] A comprehensive investigation on photo-induced oxygen vacancies was carried out by Gabel et al.[164] Figure 4-6a shows how irradiating LAO/STO with UV-light from a synchrotron under controlled molecular oxygen dosing causes the emergence and disappearance of delocalized electrons probed using photoelectron spectroscopy.[164] Recording LAO/STO samples at the Ti L edge in resonant photoemission spectra, two peaks dominate: the in-gap peak (IG) from localized carriers at ~ 1.3 eV binding energy induced by oxygen vacancies and the quasiparticle peak (QP) at Fermi level leading to the metallic behavior at the interface.[145] The strength and weight of the IG peaks increased with the exposure of X-ray, indicating that more oxygen vacancies are induced under irradiation (see Figure 4-6b). This increase in the oxygen vacancy level could be countered by supplying oxygen using a flow of O₂ to the sample during the irradiation of the synchrotron beamline. A dynamic equilibrium between the photon-induced oxygen vacancies and the supplement of oxygen could be achieved by controlling the oxygen dosing, and therefore the intrinsic properties of the heterointerfaces could be further explored by synchrotron irradiation upon minimizing the concentration of oxygen vacancies.

Chikina et al. wrote metallic conducting areas between STO and silicon using X-ray irradiation.[166] Here, light was used both to induce oxygen vacancies and conductivity in STO by transfer of oxygen from STO to Si in addition to real-time monitoring this process using photoemission. This photolithography-like approach for patterning stable metallic channels can be of interest for future oxide-based electronic devices if it can be implemented using more accessible equipment.

4.5 Perspective

The tunable photoresponsive properties of the STO-based conducting interfaces offer additional insights towards photoelectric applications. For examples, oxygen vacancy creation or acceleration of their movement by illumination provides not only an effective way to probe the on-demand properties in STO-based 2DEG systems, but also an easy way to “write” conducting channels, fabricate 2DEG devices or enhance switching speeds in memristors via light radiation. In addition, the large tunability of the conductivity at the interface when simultaneously applying light and a gate bias provides the possibility to explore the photo-controlled Rashba spin-orbit coupling and related quantum phases, as well as all-oxide spintronic devices. Furthermore, since magnetism has been observed and can be tuned by electrostatic gating in STO-based heterostructures[83,119], the question remains whether magnetism can also be conveniently induced and tailored by light. Antiferromagnetism induced using light irradiation has already been predicted in STO-based systems.[168] The antiferromagnetic order was proposed to be formed by the Pomeranchuk-type instability. However, optically induced magnetism in STO-based heterostructures remains undemonstrated.
5. Stress & strain

With the ongoing scaling of semiconductor devices, the semiconductor industry is facing several critical challenges. New device structures, new materials and strain engineering are investigated in order to improve the performance of the devices\cite{169}. The predominant focus of the industry is on biaxially stressed devices, where strain arises from stretching in two distinct directions simultaneously. Attention has also been given to uniaxial stress due to the possibility of obtaining large mobility enhancements and small shifts in transistor threshold voltages\cite{170}. Implementation of strain as a performance enhancing element has been phenomenally successful and effective since the introduction of the 90 nm technology, and uniaxial stress was successfully integrated into MOSFET processes to improve device performance\cite{171}.

In oxides, the lattice is closely coupled to the charge, orbital and spin degrees of freedom, and strain in this class of materials therefore typically has profound influence on the electrical, optical, and magnetic properties. Bulk oxide materials can often only sustain low non-hydrostatic strain lower than 1% before fracture occurs. However, advances in growth of thin films, freestanding oxide membranes and elemental substitutions present pathways to apply large, non-hydrostatic stresses.

5.1. Pathways to apply stress and measure strain: There are different pathways to apply stress to strain materials as illustrated in Figure 5-1.

- **Epitaxial strain**: Epitaxial strain occurs in thin films grown epitaxially on substrates with a lattice mismatch between the film and substrate. This typically leads to a biaxial strain where the thin film is elongated (compressed) in the plane of the film and compressed (elongated) perpendicular to the plane. By using appropriate substrates, the value of the strain can be varied and large biaxial strain of several percent can typically be achieved\cite{172}. Biaxial strain was used for example to increase the transition temperature in high-Tc superconductors and ferroelectric materials\cite{173} as well as the superconducting transition temperature in STO\cite{174}. Biaxial strain is, however, often accommodated by misfit dislocations that can partially relax the strain and cause structural and physical inhomogeneity in the films. To circumvent this problem, fully coherent, strained, extremely thin epitaxial films can be grown. By growing such ultra-thin layers on atomically smooth substrates, misfit dislocations can be avoided so that the intrinsic effect of the strain can be extracted, providing a route to achieve novel functionalities. A striking example on the interaction between a thin film and a substrate is the single monolayer of the superconductor FeSe grown on a STO substrate which leads to a dramatic enhancement of the superconducting transition temperature compared with the bulk\cite{175-177}.

- **b) Mechanical strain**: Mechanical strain occurs when external mechanical stresses are applied to a sample, for instance using a piezoelement. Typical mechanical strain devices used include (1) hydrostatic devices where isotropic stress is applied using a pressure transmitting medium, (2) a three point bending device where the sample is fixed at the ends and bend by pressing at the center and (3) uniaxial strain devices where the sample is elongated or compressed in one direction by pulling or pushing along one of the sample dimensions. Fracture often occurs at small tensile strain values, however, applying mechanical stress benefits from the possibility to dynamically tune the strain in a continuous manner. In addition, a complete study can be performed on a single sample, thereby preventing sample-to-sample variability as well as the influence of varying substrates to achieve the appropriate strain. Alternative ways to apply mechanical strain have also been demonstrated such as immobilizing the sample onto a magnetostRICTive template that exerted uniaxial stress when a magnetic field was applied\cite{178}. This was used to dynamically tune the 2DEG transport properties at the LAO/STO heterostructure\cite{178}. The uniaxial strain resulted in breaking the symmetry in the plane of the interface, which induced splitting of the electronic band structure and anisotropic conductivities.

- **c) Chemical strain**: Chemical strain can occur when modifying the lattice chemically by varying the defect level, inserting/removing elements or substituting constituent elements with elements of different sizes. This can be efficiently done in most oxides by controlling for example the density of oxygen vacancies, which tend to exert tensile strain to the lattice. This was for instance the case for PrVO$_3$ films grown on STO where the presence of oxygen vacancies resulted in straining the lattice by a few percent, leading to significant changes in the magnetic properties\cite{179}. Although large strain values can be obtained in this way, the chemical strain pathway suffers from the risk of introducing side effects not stemming from the strain itself.

- **d) Combination of strain pathways**: Combination of strain pathways may result in interesting opportunities where the drawbacks of the individual methods may be circumvented. For instance, using epitaxial and mechanical stress combined, one can explore a large strain window where the epitaxial strain is used as a large strain offset upon which the dynamical strain from the mechanical stress can operate. The combination of chemical strain and epitaxial strain was reported to result in a dynamic strain state of STO. Here, when STO was grown on top of Si, and as the top Si layer was oxidized to SiO$_2$ by post-annealing, the lattice parameters of STO changed\cite{180}.

- **e) Measurements of strain**: In order to be able to measure the strain, different techniques have been suggested including measurements of strain in thin films by X-ray diffraction\cite{181}, tensile testing of thin free-standing films\cite{182}, a capacitive strain gauge located underneath the sample\cite{183,184} and in-situ measurement of displacement in the order of nanometer during micro-tensile test for thin films by using CCD camera as a sensing device\cite{185}.
5.2. Strain and its influence on the atomic structure

Perovskite oxides, ABO₃, consists of corner-sharing BO₆ octahedra. The distortions of these BO₆ octahedra often determine the functionalities of the perovskites. However, a versatile control of the octahedral distortions is challenging as they do not respond directly to electric or magnetic fields. The control of octahedral connectivity in perovskite oxide heterostructures and their relation to strain have been discussed in Ref. [186]. Figure 5-2 shows DFT calculations on how biaxial strain influences the structure of perovskite LAO and LaNiO₃ and drastically changes the octahedral rotation as well as the metal-oxygen bond angle and bond length. The structure of STO has been also reported to be highly responsive to stress. For instance, epitaxial strain on STO films may result in a transition to a ferroelectric phase at room temperature [187] and an enhancement of the superconducting transition temperature [174] whereas strain gradients can induce a polarization by the flexoelectric effect [188]. Hydrostatic pressure has furthermore been observed to induce a cubic-to-tetragonal phase transition in STO even above room temperature as depicted in Figure 5-3 [189].

In the case of the 2DEG in STO-based heterostructures, the conductivity occurs in the Ti 3d orbitals [190]. A small change of strain can affect the occupation and overlap of the Ti 3d orbital and therefore the 2DEG carrier concentration and mobility. In addition, the octahedral may also undergo additional distortions as mentioned above that can severely affect the resulting properties.

5.3. Strain-induced changes in the electronic structure

A change in the atomic structure due to strain can also highly influence the electronic structure via changes in bond angles, bond lengths and lattice symmetries. The influence of the strain on the band structure of STO or STO-based heterostructures was studied computationally [178,191–193] as well as experimentally using angle-resolved photoemission spectroscopy using a STO single crystal bent in a three point bending [191]. As shown in Figure 5-4, the degeneracy of the dxz, dyz and dxz bands in bulk STO is lifted when the lattice symmetry is lowered using uniaxial strain.

It was also demonstrated using resonant soft X-ray linear dichroism that the out-of-plane dxz/dyz bands have a lower energy state than the in-plane dyz state in the GAO/STO heterostructure (see Figure 5-5) [172,194]. This is in sharp contrast to the heterostructure where LAO is deposited on the (001) surface of STO and the in-plane dyz state is the lowest energy sub-band. In the study by Cao et al., GAO/STO was deposited epitaxially on NdGaO₃ and TbScO₃ substrates, which caused a 1.16% compressive and 1.29% tensile strain to the heterostructure, respectively [172]. The splitting between the in-plane and out-of-plane bands were found to be highly tunable.
with compressive strain leading to an enlargement of the splitting while practically degenerate bands were observed with tensile strain.

Figure 5-5: a) Atomic structure and splitting of the bands in the GAO/STO heterostructure as deduced from DFT calculations and X-ray linear dichroism, respectively. Growing the GAO/STO heterostructure on substrates exerting b) compressive or c) tensile strain to the heterostructure results in changing the band splitting. The figure is adapted from Ref. [172].

5.4. Tuning transport properties with strain
Control over the carrier density and mobility of the 2DEG is essential for applications and may be achieved by both epitaxial, chemical and mechanical strain. Using single-crystal substrates to produce interfaces with controlled levels of biaxial strain, it was found that the carrier density and critical LAO thickness to achieve conductivity in LAO/STO was controllable (see Figure 5-6)[195]. Tensile strain prevented formation of a 2DEG at the LAO/STO interface, whereas compressive strain retained the 2DEG albeit at a lower carrier concentration and an increased critical thickness. Chen et al have also shown that it is possible to induce electrons in the CaZrO$_3$/STO heterostructure using a strain-induced polarization[196]. Here, the epitaxial strain transforms CaZrO$_3$ from being non-polar to polar, which in turn makes it energetically favorable for electrons to transfer from CaZrO$_3$ to STO and form a conducting interface. The resulting electron mobility in this heterostructure exceeded 60,000 cm$^2$/V$\cdot$s$^{-1}$ at 2 K[196].

Mechanical strain was also found to be highly effective in tuning especially the electron mobility and the carrier density[178,197–199]. When mechanically straining La-doped STO by approximately 0.3% using a three point bending device, the electron mobility at low temperatures was found to increase by 300% as shown in Figure 5-7[197]. The enhanced mobility of the electron-doped STO films under compression was suggested to occur as strain breaks the threefold $t_2g$ band degeneracy. The population of electrons in these bands then reduces the average effective mass and suppresses interband scattering[191]. The LAO/STO interface and field effect transistors made hereof were shown to exhibit an increase in the carrier density, decrease of the mobility and change in the transistor behavior upon application of hydrostatic pressure[198,199].
A new approach for mobility enhancement was proposed by applying chemical strain using defect engineering\cite{200}. Here, by means of a unique crystal engineering approach it was possible to alter the strain in Nb-doped STO films by deliberately introducing Sr vacancy clusters into the film. Films produced using this method resulted in an enhanced electron mobility exceeding 53,000 cm^2V^{-1}s^{-1}.

Application of local mechanical stress was studied using various scanning probes. It was demonstrated that the tetragonal domain walls in STO could be tuned by applying a slight pressure of the order of 10^7 Pa on a LAO/STO heterostructure using the tip of a scanning SQUID. At temperatures below 40 K, the current at the LAO/STO interface is modulated by the tetragonal domain walls\cite{86}, and applying a local stress to the domain walls was found to significantly alter the interface current distribution\cite{201}. The reconfiguration of the current distribution was suggestive of a pressure-sensitive polar state at the domain walls between the non-polar tetragonal domains. The possibility to apply local strain to affect the domain wall properties opens up for the possibility of domain walls engineering.

A large change in the local conducting properties was reported for the voltage-free tuning of LAO/STO interface conductivity at room temperature\cite{202}. Here, local electrostatic gating could be used to place the interface in a low- or high-resistive state, and following this, stress exerted by the tip of a scanning probe microscope could significantly lower the resistance of the high-resistive state (see Figure 5-8).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure5-7.png}
\caption{Figure 5-7: a) A three point bending device where compressive strain is applied on the sample surface and tensile strain is applied on the backside of the sample. b) The enhancement of the electron mobility in a compressively strained La-doped STO film grown with molecular beam epitaxy. The figure is taken from Ref. [197].}
\end{figure}

5.5. Tuning magnetic properties with strain

Despite only being the main focus of a few studies, the magnetic state of STO-based heterostructures has been shown to be highly sensitive to strain. A long-range magnetic order in LAO/STO, GAO/STO and bare STO surfaces has been observed using a scanning SQUID\cite{100}. The magnetic order was manifested as striped modulations in the magnetic field escaping the sample. The magnetic state can be tuned by applying local external forces using the tip of the SQUID, which turned the weak modulating stripes into sharp and strong stripy modulations (see Figure 5-9). When the contact was removed, the magnetic signal turned back to its initial state. As the striped modulations were oriented in the same directions as the ferroelastic domain walls of STO, the inhomogeneity was believed to originate from the tetragonal domain structure of STO and are thus present in both STO and the STO-based heterostructures. As the magnetic state couples directly to high-mobility electrons, this is particularly interesting for strain-dependent spintronic studies.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure5-8.png}
\caption{Figure 5-8: a) Schematic illustration of the scanning tip pressed onto the LAO/STO heterostructure. b) The local resistance of the LAO/STO interface after positive gate voltage (black line), negative gate voltage (red line) and when applying different forces mechanically to the high-resistive state. The figure is taken from Ref. [202].}
\end{figure}

Figure 5-9: Magnetic stripes in GAO/STO observed using scanning SQUID at 15 K. Hovering the tip of the scanning SQUID in non-contact mode above the sample resulted in a map of a weakly modulating magnetic field escaping the sample (lower part of the figure). However, when the tip is in contact mode and apply stress to the sample surface, strong and sharp modulations are observed (upper part of the figure). \(\Delta \Phi\) denotes the peak-to-peak amplitude of the magnetic stripes. The figure is taken from Ref. [100].

In a prior study, a strain dependence of the magnetic state was observed in LAO/STO using a similar scanning SQUID\cite{203}. Here, the magnetic state was found to be resolution-limited ferromagnetic
patches rather than a long-range magnetic order (see Figure 5-10). The magnetization of the ferromagnetic patches was found to change direction and magnitude upon touching with the tip of the SQUID. Unlike the ordered magnetic stripes, the final state remained stable when the contact was removed.

**Figure 5-10**: Ferromagnetic patches observed in LAO/STO using scanning SQUID as a function of scan number where in each scan the tip of the SQUID is in contact with the sample surface (upper panel) or hovering above the surface in non-contact mode (lower panel). The signal is the magnetic flux (measured in m\(\phi_0\)) in the scanning SQUID pick-up loop, which reflects the magnetic field produced by the sample. The figure is adapted from Ref. [203].

A few theoretical studies address the effect of strain on the magnetic properties in STO using DFT[204,205]. In a study performed by Zhang et al it was calculated that oxygen vacancies in STO lead to a non-zero magnetization in absence of an applied stress, consistent with experimental results[5]. The magnetization diminished as a positive hydrostatic pressure of 30 GPa was applied, however, a high-spin state was predicted when applying a negative hydrostatic pressure of -10 GPa (see Figure 5-11). In agreement with the local strain experiments, the strain could therefore be used to switch the magnetization on and off.

**Figure 5-11**: The pressure dependence of the magnetic moments in a 2x2x2 unit cell large supercell of oxygen deficient STO. The figure is taken from Ref. [204].

5.6. Perspective

One of the challenges for attaining epitaxial strain in the lab is the limited number of substrates available. Therefore, only a discrete number of different strain values can be achieved. Introducing strain by epitaxial growth is therefore only a viable option if substrates with the required mismatches are available and, equally important, if variations in substrate and epitaxial film quality (impurities, surface defects, crystal miscut angles etc.) can be avoided as these can destroy the desired properties entirely. These drawbacks are to a large extent avoided when using mechanical strain, however, the fragility of oxides often severely limits the achievable strain values. An epitaxial STO template layer grown on Si by molecular beam epitaxy (MBE) or pulsed laser deposition (PLD) seems not only to be able to bridge oxides and semiconductors[206,207], but as thin Si substrates are flexible, it also provides a pathway for achieving large mechanical strain in STO. In another work, a general method to create freestanding oxide heterostructure membranes was reported[208]. This was done using a sacrificial layer of Sr\(_3\)Al\(_2\)O\(_6\) thin film which act as a template for epitaxial perovskite growth and was subsequently dissolved by water to form freestanding oxide membranes. It was shown that it was possible to transfer millimeter-size single crystalline La\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\)/STO superlattices onto Si. The physical properties of the layers were preserved, or even enhanced, in terms of the Curie temperature and residual resistivity[208]. Using such membranes one can envision that a large strain may be achievable either by placing the membranes on a flexible substrate or performing strain studies on a freestanding membrane.

The tetragonal domain walls of STO has attracted more attention recently as they may be used to control the 2DEG properties at the nanoscale. This is particularly interesting as the domain walls have different magnetic[100], polar[201] and current carrying[86] properties. Moreover, as the domain walls separate tetragonal domains with the unit cell elongated in the x, y or z-direction, strain is expected to couple directly to the domain landscape with the potential of designing writable, erasable and movable nanoelectronics. Strain may not only be used as a tuning knob for already grown STO-based heterostructures. Defects and in particular oxygen vacancies play an important role in the resulting properties of the heterostructures. These defects exert a positive or negative stress to the surrounding lattice, and their formation energy will thus be dependent on the stress applied to the sample[204]. During a typical growth of STO-based heterostructures, it should therefore be possible to control the defect level by applying mechanical stress to the sample. If the defects are kinetically trapped after the growth, releasing the strain may thus lead to strain-induced permanent tuning of the properties.
6. Other factors: Adsorbates, particle bombardment and temperature:

The previous sections serve as an overview of the major pathways used to tune the properties of STO-based heterostructures via external stimuli. However, these pathways are far from encompassing all studies where external stimuli have been shown to change interface properties of STO-based heterostructures. In this section, we discuss how the interface properties can be changed by additional factors such as 1) interaction between the oxide surface and liquid/gaseous adsorbates, 2) bombardment of high-energy particles and 3) temperature cycles at elevated temperature or across low-temperature structural phase transitions. This paves the way for producing nanosized electronic circuits, tuning the interface properties with real-time monitoring during growth and using the STO-based heterostructures for molecular sensing applications.

6.1. Liquid/gaseous adsorbates:

In this section, we will cover the literature where the explicit effect of adsorbates was studied on the interface conductivity in STO-based heterostructures.

a) Controlling the interface conductivity using surface adsorbates

Due to dangling bonds of apical atoms at the LAO surface in LAO/STO heterostructures, the surface is highly susceptible for adsorption or even chemical binding with molecules present on the surface. As the heterointerface often is near the oxide surface, there consequently exists an intimate relationship between the nature of the adsorbed surface molecules and the interface conductive state. The relation has been explicitly investigated by several studies. Dai et al. showed that it possible to control the local oxygen surface content by oxygen plasma bombardment (see Figure 6-1)[209]. It was found that areas exposed to the oxygen plasma were rendered insulating thus providing a convenient pathway to pattern the interface conductivity by protecting selective areas with resist. Specifically, it was found that exposure to oxygen plasma left the LAO surface highly hydroxylated that due to the chemical binding of the hydroxyl group displayed a good degree of stability at room temperature and ambient conditions[209].

Figure 6-1 (left panel) Electrostatic force microscopy phase image of a LAO/STO device exposed to the oxygen plasma with dark orange corresponding to regions with interface conductivity. (right panel) Schematic illustration of hydroxyl termination at the LAO surface and extent of the 2DEG after exposure to oxygen plasma. The figure is taken from Ref. [209].

Dai et al. later found that by scanning the LAO surface using the tip of a conducting AFM biased with a negative voltage at room temperature, the interface conductivity could be locally erased (see Figure 6-2 and Section 2)[210]. Upon dispersing a polar solvent such as isopropanol on the sample surface, the interface metallic state could be recovered.

Figure 6-2 (left panel) Relative contribution of the LAO/STO interface charge density from surface adsorbates (n_{surf}) and oxygen vacancies doping (n_{ov}) in stable (solid circles) and metastable (dashed circles) states. (middle panel) Interface conductance measured between two contacts as a function of time with the c-AFM scanning and polar solvent dispersion indicated at ‘1’ and ‘2’, respectively. (right panel) Schematic illustration of the working principle behind the polar adsorbate interface doping. The figure is taken from Ref. [210].

By probing the Ti valance state using in-situ XPS, it was possible for Scheiderer et al. to pinpoint the linkage between the density of interface charge carriers and the presence of surface adsorbed atomic hydrogen from molecular hydrogen as well as water[211]. The authors demonstrated reversible cycling of this n-type doping with surface adsorbed atomic hydrogen (see Figure 6-3).

Figure 6-3 The spectral weight ratio between Ti^{3+} and Ti^{4+} (plusses) as well as relative Al 2p core level shift (circles) in a LAO/STO heterostructure measured with XPS as a function of in-situ experimental conditions. The figure is taken from Ref. [210].

Several additional studies have investigated the effect on the LAO/STO conductivity when exposing the LAO surface to water droplets[212], water moisture[213,214] and acids[154]. Brown et al. showed that whereas the change in the resistance upon immersion was poorly correlated with the permittivity of the solvent, a good correlation was found with the strength of the acids (see Figure 6-4)[154]. Here, weak acids with a high proton affinity were found to drive the interface conductivity towards an insulating state. This was attributed to a lowering of the proton concentration on the sample surface thereby removing the attractive forces confining the electrons to the interface. This led to an increase in the resistance in analogy to removing a positive top-gate potential.

Figure 6-4 (left panel) Relative contribution of the LAO/STO interface charge density from surface adsorbates (n_{surf}) and oxygen vacancies doping (n_{ov}) in stable (solid circles) and metastable (dashed circles) states. (middle panel) Interface conductance measured between two contacts as a function of time with the c-AFM scanning and polar solvent dispersion indicated at ‘1’ and ‘2’, respectively. (right panel) Schematic illustration of the working principle behind the polar adsorbate interface doping. The figure is taken from Ref. [210].

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conditions with the sample being exposed to either photons (light) or surface adsorbates (water). The figure is taken from Ref. [154].

**Figure 6-4** Ratio of the resistance of LAO/STO samples after two-minute immersion in different solvents, \( R_0 \), relative to the initial resistance, \( R_i \), plotted as a function of the solvent permittivity (left panel) and \( pK_a \), of the protonated solvents (right panel). The solvents are: toluene (TOL), tetrahydrofuran (THF), dichloromethane (DCM), acetophenone (ACO), acetaldehyde (ACA), ethanol (EtOH), nitromethane (MeNO₂), dimethylformamide (DMF), acetonitrile (MeCN), water (H₂O) or formamide (Form). The figure is taken from Ref. [154].

**b) Reversible metal-to-insulator transition using a combination of adsorbates and additional stimulus**

A few studies have investigated the effects of combining additional external stimuli with the presence/absence of surface adsorbed species. It was found by Brown et al. that an insulating LAO/STO heterostructures prepared by deprotonation from surface adsorbed water could be rendered conductive by irradiation with photons at room temperature (see Figure 6-5)[154]. This insulator-to-metal transition may share similarities with the previous discussed effect of light irradiation and application of electric fields from e.g. a back-gate (see Section 2), however, this needs to be elucidated further.

**Figure 6-5** The resistance of LAO/STO as a function of sample conditions with the sample being exposed to either photons (light) or surface adsorbates (water). The figure is taken from Ref. [154].

**c) Origin of the adsorbate effect**

As it can be seen from the above-mentioned studies, underpinning the mechanism of how the adsorbed species directly affects the interface electron doping level is not trivial. Nonetheless, by systematically studying the influence of surface adsorbed water with almost the entire family of existing STO-based conducting heterointerfaces, Zhang et al. identified surface oxygen vacancies as playing the central role[215]. The authors argued that water chemistry at surface oxygen vacancies serves as a common mechanism for supplying electrons to the interface for all the investigated heterointerfaces. The formation energy of these surface oxygen vacancies in the particular oxide thin film would dictate the concentration of chemically bound water molecules (i.e. hydroxyl-groups) as well as the robustness of interface conductivity when the samples where exposed to oxygen annealing (see Figure 6-6). This study provides an auxiliary explanation to the origin of interface conductivity in STO-based heterostructures, complementing the existing explanations based on polarity-induced spontaneous oxygen vacancy formation at the top surface[18] and adsorbate-induced changes in the conductivity[154,211,214].

**Figure 6-6** a) Rough ranking of conductivity stability at different STO-based heterointerfaces when subjugated to oxygen annealing at temperatures between 300-600 °C. b) The estimated energy difference (\( E_{diss} \)) between shallow surface levels at the top film surface and the Fermi energy of STO, plotted as a function of robustness to oxygen annealing. The figure is taken from Ref. [215].

### 6.2. Particle bombardment:

Particles with high kinetic energies impacting the surface of STO or STO-based heterostructures can lead to intentional or unintentional incorporation of elements, formation of defects or activation of chemical processes. Particle bombardment may occur in-situ during the deposition of thin films or ex-situ after the sample synthesis by an external energetical particle source.

**a) Effect of particle bombardment during PLD growth:**

Heterostructures are often synthesized using pulsed laser deposition of thin films on a single crystalline STO substrate. In this deposition process, the laser impacts a target that ablates into a plasma comprised of particles traveling with kinetic energies on the order of tens of electron volts. The high kinetic energies enables the epitaxial growth of crystalline films on STO even at room temperature[216], but it may also cause defects as well as interdiffusion of particles between the top film and STO. Sambri et al. investigated the effect of depositing LAO at room temperature on STO in an atmosphere of argon or oxygen with varying pressures[217]. The room temperature deposition of LAO results in an amorphous phase, and the primary driver for obtaining conducting interfaces is the transfer of oxygen from STO to the oxygen-deficient LAO film. Increasing the oxygen partial pressure in the deposition increases the interaction between the plasma and the background oxygen gas, resulting in both a lowering of the kinetic energy and an increased oxidation of the plasma plume species. At low oxygen deposition pressures, the interfaces were therefore conducting, but at pressures of approximately 10⁻¹ mbar or above, the interfaces were insulating (see Figure 6-7). Replacing the oxygen gas with argon, however, resulted in approximately the same lowering of the kinetic energy, but without a significant plume oxidation. In this case, depositing in an argon pressure of 10⁻³ mbar produced conducting interfaces, signifying the importance of the oxidation state of the plasma plume. A metal-to-insulator transition occurred at an argon pressure of 10⁻¹ mbar, and by measuring the...
kinetic energy if was proposed that a minimum kinetic energy on the order of 1 eV was needed to kinetically activate the transfer of oxygen from STO to LAO at room temperature. In this picture, the particle bombardment was necessary to activate the redox reaction causing the formation of oxygen vacancies and conductivity at the interface.

Several studies also investigate the effect of the particle bombardment along with other stimuli occurring during the pulsed laser deposition\[136,211,218–221\]. This can be done by measuring the conductivity of the STO-based heterostructure in real-time during the deposition. This shed light on the origin of conductivity in heterostructures with top films deposited on STO at room temperature. It was well-established that conductivity was observed ex-situ only above a critical top layer thickness for LAO/STO and GAO/STO, but not at the interface of La\(_{7/8}\)Sr\(_{1/8}\)MnO\(_3\)/STO independent of the top layer thickness\[7,222\]. It was inferred that oxygen transfer from STO to the top film was paramount for the conductivity. Measuring the conductivity during the deposition, however, revealed that conductivity was established after the first few laser pulses, much earlier than the critical thickness (see Figure 6-8). Using oxygen dosing in the deposition chamber, the discrepancy between the results obtained in-situ and ex-situ was investigated. The discrepancy was attributed to annihilation of oxygen vacancies in STO in the case where deposited material on STO was insufficient to protect the oxygen vacancies from molecular oxygen in the atmosphere. Surprisingly, deposition of La\(_{7/8}\)Sr\(_{1/8}\)MnO\(_3\) was also found to induce conductivity initially due to formation of oxygen vacancies caused by the bombardment of the plasma particles. Thus, the resulting conductivity was found to be a competition between several mechanisms: particle bombardment, oxygen transfer across the interface, oxygen annealing and (to a small extent) UV-radiation from the plasma plume.

**Figure 6-7:** (top panel) Sheet conductance of the amorphous-LAO/STO interface as a function of deposition pressure during a pulsed laser deposition in either oxygen or argon. The sheet conductance is measure ex situ after the samples are taken out of the deposition chamber. (bottom panel) Schematic illustration of the process for creating conducting interfaces. If the top film is oxygen deficient and is deposited at room temperature using plasma species with sufficient kinetic energy, a transfer of oxygen from STO to the top film can occur. This leads to oxygen vacancies and itinerant electrons at the STO side close to the interface. The figure is taken from Ref. \[217\].

**Figure 6-8:** The temporal dependence of the sheet resistance measured in-situ during the pulsed laser deposition of various films on a STO substrate. The figure is taken from Ref. \[218\].

b) Effect of ex-situ particle bombardment:
Following the removal of the STO-based heterostructure from the pulsed laser deposition growth chamber, ex-situ particle bombardment has likewise been demonstrated to constitute a convenient pathway for altering the interfacial state. It is well established that bulk insulating STO may be rendered three-dimensionally metallic conductive if subjugated to bombardment by ionic species under vacuum even at room temperature\[223\]. This transformation from insulator to metal is driven by the prevalent formation of oxygen vacancies throughout the STO lattice that correspondingly \(n\)-type dope the system. By carefully controlling the energy of incoming ionic species from an Ar\(^+\) source, Aurino *et al.* found that originally metallic LAO/STO heterostructures could be rendered insulating in a narrow window of irradiation times (see Figure 6-9)\[224\]. This method represents an effective pathway for patterning the interface conductivity by covering selective areas of the LAO/STO heterostructures with e.g. polymer resists during the Ar\(^+\) irradiation.

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The mechanism for this persistent metal-to-insulator transformation of the LAO/STO heterointerface was further investigated by Aurino et al. [225]. Here it was concluded that the Ar⁺ irradiation leaves a progressively growing layer of amorphous-LAO on top of the LAO/STO heterointerface (see Figure 6-10). When the thickness of crystalline LAO this way is reduced below the critical thickness for interface conductivity of 4 u.c., the metal-to-insulator transition occurs. However, it was found in the study that the process indeed is reversible by high-temperature annealing in oxygen whereupon the amorphous-LAO recrystallizes thus rendering the interface metallic again.

The effects of Ar⁺ ion bombardment is not limited to microstructure changes as etching of the top layer readily can occur as well. Ridier et al. studied the effects of Ar⁺ cluster ion bombardment [226]. The authors of this study uncovered the dynamical effects occurring during the Ar⁺ ion bombardment and found that despite the entire LAO top-layer being removed during the bombardment, the STO below remained conductive in the near-surface region following ion exposure. Moreover, the authors elucidated that the lateral effects of the ion exposure extend up to several millimeters away from the irradiated area [226] (see Figure 6-11). Finally, the authors show that high-temperature annealing in oxygen to a large extent could reverse the effects to interface conductivity of Ar⁺ cluster ion bombardment.

6.3. Temperature-induced changes:

The temperature has a dramatic effect on the properties at STO-based interfaces and in particularly on the conductivity and electron mobility, which have both been reported to increase by up to four orders of magnitude when cooling down from room temperature to 2 K [20,110]. In most cases the properties change reversibly as the temperature is varied. Noticeable exceptions include the cases where the temperature is elevated with respect to room temperature to activate oxygen diffusion in the lattice or when crossing the 105 K phase transition of STO between a cubic and tetragonal crystal structure [227].
The change in sheet resistance of STO-based heterostructures with respect to time under different room temperature storage conditions and top layer thicknesses. The figure is taken from Ref. [228].

### a) Annealing at elevated temperatures:

Annealing in the presence of molecular oxygen has frequently been used to minimize the amount of oxygen vacancies in oxides as well as to test the influence of such vacancies, however, with the risk of inducing cation movement and cation vacancies[229]. In an elaborate study, Gunkel et al. measured the conductivity of a range of STO-based heterostructures with varying top films at 950 K while varying the oxygen partial pressure [230]. These high temperature equilibrium conductance measurements were used to determine whether the interface conductivity originated from thermally unstable oxygen vacancies or had annealing resistant contribution, as expected if the conductivity arises from the polarity of the top film. In this way, the interface conductivity in amorphous-LAO/STO and GAO/STO was attributed to oxygen vacancies, whereas the conductivity in crystalline-LAO/STO, NdGaO$_3$/STO and (La,Sr)(Al,Ta)O$_3$/STO scaled with the top film polarity and was attributed to stem from the polarity. This suggested that the GAO film is overall non-polar possibly due to an inhomogeneous distribution of aluminum vacancies[231]. For the heterostructures where the conductivity is formed by oxygen vacancies, the conductivity was found to weakly degrade over time at ambient conditions[228]. The degradation ($\delta R_s/\delta t$, see Figure 6-12) could be minimized by storing the samples in oxygen deficient environment or lowering the oxygen diffusion through the top film by increasing the layer thickness or utilizing a material with a high oxygen diffusion barrier such as GAO[22,228].

The case of GAO/STO with a GAO film thicker than 1-2 nm is particularly interesting, as the conductivity here is stable at room temperature on the time scale of years at ambient conditions, but by elevating the temperature to 200-300 °C the conductivity could be tuned to a desired level[22]. This is depicted in Figure 6-13 where GAO was deposited by pulsed laser deposition at an oxygen partial pressure of $10^{-5}$ mbar resulting in an initial sheet carrier density of around $2 \times 10^{14}$ cm$^{-2}$. Annealing in pure oxygen at ~200 °C resulted in a controlled decrease of the carrier density and eventually a metal-to-insulator transition. This change in the resistance was used to enable conducting AFM writing of nanocircuits as discussed in Section 2. Writing of nanocircuits was initially unsuccessful using an as-deposited GAO/STO heterostructure[22]. However, after raising the resistance of the same sample to an insulating state using annealing on a hot plate in ambient conditions, conducting AFM writing was possible[22].

Annealing also has a drastic effect on the low temperature properties. A curiously example was reported in the GAO/STO heterostructure[167]: Whereas the room temperature conductivity, electron mobility and carrier density of GAO/STO remained stable during 6 months of sample storage in a vacuum desiccator, the low temperature properties were observed to change (see Figure 6-14). After storage, both the sheet conductance and electron mobility at 2 K increased by roughly a factor of four. This dynamical mobility enhancement was proposed to originate from a redistribution of oxygen vacancies that minimizes the number of collisions between itinerant electrons and oxygen vacancy scattering sites.
6.4. Perspective

Several interesting perspectives exist for the external stimuli discussed in this section. The changes in the properties of the interface conductivity in STO-based heterostructures can in general be used for sensing the external stimuli applied to the sample. This is particularly the case of the influence of surface adsorbates, which in principle may be envisioned to design gas detectors. By varying the top film material, one may get different responses to different gaseous species, which could lead to selectivity in the detection. The real-time monitoring of the conductivity in STO-based heterostructures offers the potential for tailoring the conductivity on-the-fly by in-situ switching from one target to another or by varying the deposition conditions. Combined with other in-situ characterization techniques such as reflective high-energy electron diffraction (RHEED) and X-ray photoelectron spectroscopy (XPS), this is powerful method for achieving the desired properties of heterostructures. In particular, one can tune the properties in real-time by varying, e.g., the kinetic energy for the impacting plasma species, alter the reducing or oxidizing properties of the capping layers and modulate the crystallinity of the top film. The in-situ conductivity measurements can also be combined with the annealing in order to make an even more versatile tuning of the properties.
7. Conclusion and perspectives

The increasing demand for new materials with combined new and targeted functionalities realizable in, e.g., oxides\textsuperscript{235}, requires the control of microstructure and architecture at the nanoscale. This has been done for many years using nano-engineering. Another way which has the potential to make a significant impact in a multitude of diverse areas within materials science is modifying the materials by applying external stimuli such as light, temperature, magnetic fields, electric fields and stress.

The available functional perovskite oxide thin film materials, such as STO, offers a close interaction between the lattice, spin, charge and orbital degree of freedom and the possible to confine the conductivity in two, one or zero dimensions. Traditionally, the search for new functional bulk materials involves also the influence of additional single external stimulus where the materials properties can be modified within a particular parameter space dictated by the stimulus. This offers additional external control over properties and nanostructure of materials enabling the production of multifunctional devices with unique properties, ranging from “writing” a conducting channel (Section 2) and fabricating 2DEG devices via X-ray radiation (Section 4), spintronic devices where magnetism is induced by light (Section 4), selective detection of gases (Section 6) and controlling the level of defects in real-time during growth (Section 6).

Within the research framework of surfaces and interfaces of oxides, the question remains on how a material will respond when not only a single stimulus is applied at the time, but rather multiple stimuli are applied. This research topic is to a large extent still unexplored both experimentally and theoretically. Navigating this multi-dimensional space in search of functional materials with improved properties is an enormous task without an additional guidance. Therefore, computational materials science is one of the key tools for understanding the responds of materials to multiple stimuli. Adding multiple external stimuli to surfaces and interfaces where broken symmetry, reduced dimensionality, atomic relaxations and intermixing of atoms occur at the interface can substantially affect the magnetic and transport properties of these materials. This provides another dimensionality to the richness of stable or metastable states that oxide surfaces and interfaces may display depending upon their environment.

We believe that a theory-driven intelligent approach is imperative for efficiently identifying and understanding the role of single and even multiple stimuli interaction. In addition to understanding the microscopic origins of the coupling mechanisms, the other most immediate task is to understand the role of micro- or nanostructure when such a coupling occurs. Finally, compared to responds from a single stimulus material, applying multi-stimuli is a fascinating way to achieve finer modulations of the materials through a larger parameter space. Inspired by these, the next challenge is to transfer the findings of single and multiple stimuli into applications to open up new technologies and markets opportunities.
8. Acknowledgements

The authors gratefully acknowledge F. Gunkel and A. Smink for suggestions and fruitful discussions as well as proofreading of the review. D.V. Christensen and N. Pryds would like to thank the support by the NICE project, which has received funding from the Independent Research Fund Denmark, Grant No. 6111-00145B. F. Trier acknowledges support by research grant VKR023371 (SPINOX) from VILLUM FONDEN.

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