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Conductance and gating effects at sputtered oxide interfaces

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Conductance and Gating Effects at Sputtered Oxide Interfaces

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About the cover: The cover shows an illustration of the $\text{LaAlO}_3/\text{SrTiO}_3$ interface. The left side is the LaAlO_3 film and the right side is the SrTiO_3 substrate. The light blue, dark blue, orange, red and gray spheres represent La, Al, Sr, Ti and O atoms, respectively. The light gray squares represent oxygen octahedra.

To my grandfather

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1

Introduction

1.1. Complex oxides

The semiconductor-based transistor launched a revolution in electronics when it was invented at Bell lab in 1947. Silicon integrated circuits are the foundation of basically everything we take for granted now in our daily life. Nevertheless, silicon electronics faces a challenge: the latest transistor is only 7 nm wide, and further shrinking the size would lead to unstable behavior. This challenge requires redesign and more advanced devices, or looking for alternative materials to silicon.

Complex oxide materials offer scientists and engineers a theme park of new physics. They exhibit a wide range of novel functionalities which cannot be achieved in conventional semiconductors, including colossal magnetoresistance, high-temperature superconductivity, metal-insulator transitions, and multiferroicity [1]. A complex oxide contains oxygen and at least one other element, which is usually from the transition metal group. In many complex oxides, the electrons are strongly correlated [2, 3]. Their rich phenomena arise from the complex interplay between the charge, orbital, lattice and spin degrees of freedom, as illustrated in Fig. 1.1(a).

In the complex oxides family, perovskites with the chemical formula ABO_3 have received a remarkable amount of attention. The crystal structure of an ideal perovskite oxide is sketched in Fig. 1.1(b). This structure possesses an extraordinary chemical flexibility – most of the elements found in the periodic table can be placed on the A or B sites [4]. The ideal cubic structure is rare in nature and usually undergoes symmetry-lowering distortions depending on the size of the A and B cations. The deviation from the ideal

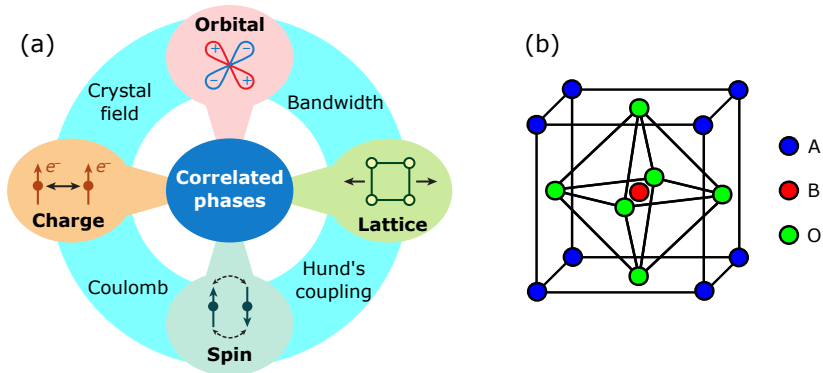


Figure 1.1: (a) The interplay between charge, orbital, lattice and spin degrees of freedom gives rise to correlated phases in transition metal oxides. Image reprinted from Ref. [3]. (b) The crystal structure of an ideal perovskite oxide, ABO_3 . The blue, red and green spheres represent the A, B, and O atoms, respectively.

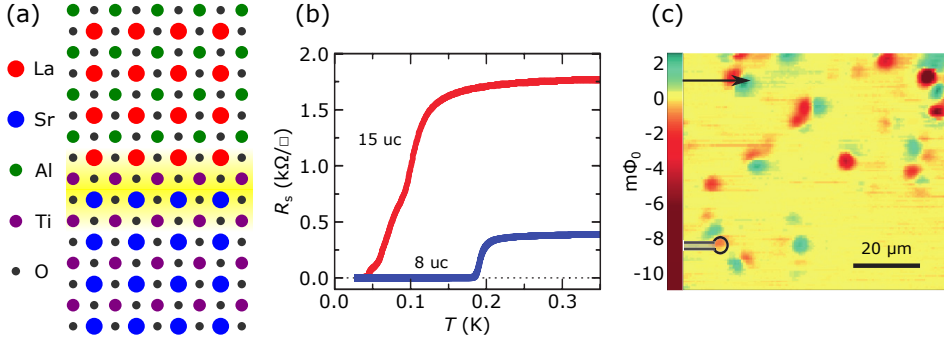


Figure 1.2: (a) Sketch of the $\text{LaAlO}_3/\text{SrTiO}_3$ interface. The yellow area represent the 2DES. (b) Sheet resistance (R_s) as a function of temperature of samples with LaAlO_3 thicknesses of 8 and 15 unit cells, showing the occurrence of superconductivity. Image adapted from Ref. [6]. (c) Scanning SQUID image mapping the ferro-magnetic order in $\text{LaAlO}_3/\text{SrTiO}_3$. The inset shows the SQUID pick-up loop for sensing magnetic flux and the arrow denotes the fast scan axis and the SQUID orientation. Image adapted from Ref. [7].

structure can be quantified by the Goldschmidt tolerance factor [5]

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}, \quad (1.1)$$

where r_A , r_B and r_O are the ionic radii of the A, B and O ions, respectively. The richness of physical properties exhibited by perovskite oxides is closely related to the diversity of structural distortions in these materials.

1.2. $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures

In his Nobel lecture, Herbert Kroemer coined the famous phrase that "the interface is the device" [8]. During the past decades, advancements in thin film growth technology have enabled the fabrication of oxide heterostructures with atomic precision. A landmark work appeared in 2004, in which Ohtomo and Hwang reported a high-mobility two-dimensional electron system (2DES) at the interface between LaAlO_3 and SrTiO_3 [9]. A sketch of the $\text{LaAlO}_3/\text{SrTiO}_3$ interface is given in Fig. 1.2(a). Both materials are band insulators in bulk, with band gaps of 5.6 eV and 3.25 eV for LaAlO_3 and SrTiO_3 , respectively. Therefore the discovery of this conductive interface with a mobility exceeding $10^4 \text{ cm}^2/\text{Vs}$ is indeed remarkable. Ever since then the $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructure has generated an enormous amount of research interest in the oxide community.

In the past 15 years, scientists have observed many other intriguing properties beyond conductivity at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface, such as superconductivity, magnetism and even their coexistence. Superconductivity was first reported by Reyren *et al.* [6] as shown in Fig. 1.2(b). They found that the superconducting transition temperature is

about 200 mK and the thickness of the superconducting layer is approximately 10 nm.

LaAlO_3 and SrTiO_3 are both non-magnetic materials. It was quite surprising when Brinkman *et al.* [10] first reported magnetism at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface. They observed a Kondo-like resistance minimum and a hysteretic magnetoresistance, although the hysteresis was later found to be a measurement artifact. To date, signatures of magnetism have been observed by many different measurement techniques, such as superconducting quantum interference device (SQUID) [11], magnetic torque magnetometry [12], scanning SQUID [7, 13, 14] as shown in Fig. 1.2(c), x-ray magnetic circular dichroism [15, 16], magnetic force microscopy [17] and magnetotransport measurement [18–20]. However, the reported results are inconsistent and a convincing physical picture for the origin of the magnetism is still lacking.

1.3. Mechanisms for interfacial conduction

The physical mechanism responsible for the formation of the 2DES at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface has been a highly debated topic since its discovery. A proper explanation which can cover all the experimental observations is still lacking. Proposed mechanisms basically fall into two categories, namely intrinsic and extrinsic mechanisms. The intrinsic mechanism considers the polar discontinuity between the polar LaAlO_3 and the non-polar SrTiO_3 . The extrinsic mechanisms involve the roles of different defects which are formed during film growth. In this section, we introduce these mechanisms and briefly discuss their limitations. More detailed information can be found in recent review articles [21, 22].

1.3.1. Intrinsic mechanism: polar discontinuity

In their seminal paper, Ohtomo and Hwang proposed that the polar discontinuity at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface is the dominant mechanism for conductivity [9]. This mechanism was later discussed in detail by Nakagawa *et al.* [23] in the polar catastrophe model, which is illustrated in Fig. 1.3. In the [001] direction, a perovskite oxide, ABO_3 , can be considered as alternating stacks of AO and BO_2 planes. SrTiO_3 consists of neutral $\text{Sr}^{2+}\text{O}^{2-}$ and $\text{Ti}^{4+}\text{O}_2^{4-}$ planes, whereas LaAlO_3 consists of charged $\text{La}^{3+}\text{O}^{2-}$ and $\text{Al}^{3+}\text{O}_2^{4-}$ planes, carrying formal +1 and –1 charges, respectively. Depending on SrTiO_3 surface termination, two types of interface can be obtained: the LaO/TiO_2 interface (Fig. 1.3(a)) and the AlO_2/SrO interface (Fig. 1.3(b)). In both cases, the alternating net charges (ρ) in LaO and AlO_2 planes produce an electric field (E), leading to a diverging electric potential (V) as the thickness of LaAlO_3 layer increases, which is known as the polar catastrophe [24, 25]. In order to prevent the catastrophe, the system undergoes different types of interfacial reconstructions. For the LaO/TiO_2 interface, an electronic reconstruction

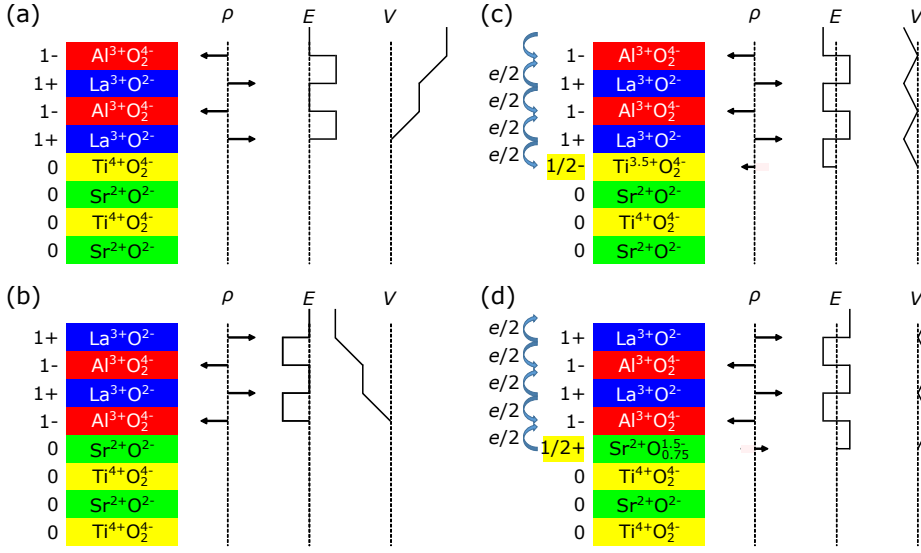


Figure 1.3: An illustration of the polar catastrophe model for atomically abrupt (001) interfaces between LaAlO_3 and SrTiO_3 . (a) The unreconstructed interface has neutral (001) planes in SrTiO_3 , but the (001) planes in LaAlO_3 have alternating net charges (ρ). If the interface plane is LaO/TiO_2 , this produces a non-negative electric field (E), leading in turn to an electric potential (V) that diverges with thickness. (b) If the interface is instead placed at the AlO_2/SrO plane, V diverges negatively. (c) The divergence catastrophe at the LaO/TiO_2 interface can be avoided if half an electron is added to the last TiO_2 plane. This produces an interface dipole that causes E to oscillate about 0 while V remains finite. (d) The divergence for the AlO_2/SrO interface can also be avoided by removing half an electron from the SrO plane in the form of oxygen vacancies. Image adapted from Ref. [23].

occurs by transferring half an electron per unit cell from LaAlO_3 to SrTiO_3 (Fig. 1.3(c)), resulting in an n -type interface where half of the Ti^{4+} ions becoming Ti^{3+} . In the same manner, a p -type interface should be formed for the AlO_2/SrO interface. This can be achieved through an atomic reconstruction, namely oxygen vacancies formation in the SrO layer (Fig. 1.3(d)).

A robust support for the polar catastrophe model is that interfacial conduction only occurs when the LaAlO_3 layer exceeds a critical thickness of 4 unit cells [26]. At the critical point, the valence band at the LaAlO_3 surface crosses the SrTiO_3 conduction band at the interface, resulting in the charge transfer. Therefore, altering the polarization of the LaAlO_3 layer should alter the critical thickness. This has been experimentally demonstrated by Reinle-Schmitt *et al.* [27] by diluting LaAlO_3 with SrTiO_3 , forming $(\text{LaAlO}_3)_x(\text{SrTiO}_3)_{1-x}/\text{SrTiO}_3$ interfaces. The critical thickness increases with decreasing x .

On the other hand, there are a number of experimental observations that the polar

catastrophe model fails to explain. First, it predicts a p -type interface for SrO-terminated SrTiO₃, however this interface is always found to be insulating [9]. Second, the model requires a charge transfer of half an electron per unit cell, which correspond to a carrier density of $3 \times 10^{14} \text{ cm}^{-2}$. But experimentally measured carrier densities are usually one order of magnitude lower [28–30]. Third, the core-level shift of LaAlO₃ measured by x-ray photoemission spectroscopy is much smaller than the value predicted by the polar catastrophe model [31–35]. Moreover, the shift is independent of the LaAlO₃ thickness, which is against the electronic reconstruction picture involving a cumulative shift of the LaAlO₃ valence band above the SrTiO₃ conduction band [34]. Fourth, conductivity has been also observed at interfaces where polar discontinuity does not exist, such as amorphous LaAlO₃ on SrTiO₃ (001) [36] and crystalline LaAlO₃ on SrTiO₃ (110) [37, 38].

1.3.2. Extrinsic mechanisms: roles of defects

It is important to note that the polar catastrophe model considers an ideal LaAlO₃/SrTiO₃ interface as shown in Fig. 1.4(a). However, it is practically impossible to obtain such a defect-free interface. A real interface contains various types of defects, whose influences on interfacial conduction should not be neglected [39]. Here, we discuss three main defect-driven mechanisms.

The first extrinsic mechanism for generating carriers is the formation of oxygen vacancies as depicted in Fig. 1.4(b). Oxygen vacancies are the most abundant defects in SrTiO₃, which greatly affect the electronic, magnetic and optical properties. They can be easily introduced by annealing SrTiO₃ in a reducing atmosphere, and give rise to even superconductivity [40]. In LaAlO₃/SrTiO₃ heterostructures, the concentration of oxygen vacancies depends on the temperature and oxygen pressure during growth [41–43]. They can be significantly removed by post oxygen annealing [44–46]. Using a conducting-tip atomic force microscope, Basletic *et al.* [44] directly measured the thickness of the 2DES to be $\sim 7 \text{ nm}$ after high oxygen pressure annealing. On the other hand, theoretical works have predicted that oxygen vacancies formed at the LaAlO₃ surface can also be a possible source of electrons for the 2DES [47, 48].

The second extrinsic source of electrons is La/Sr intermixing as shown in Fig. 1.4(c). It has been known that La-doped SrTiO₃ is metallic due to the replacement of Sr²⁺ by La³⁺ [49]. La/Sr intermixing at the LaAlO₃/SrTiO₃ interface has been experimentally observed by electron energy loss spectroscopy [23], surface x-ray diffraction [50] and medium-energy ion spectroscopy [51].

The third extrinsic origin for interfacial conduction is LaAlO₃ stoichiometry. To date, LaAlO₃/SrTiO₃ heterostructures are commonly prepared by pulsed laser deposition (PLD). A fundamental premise that justifies the use of PLD is the stoichiometric transfer of materials from the target to the film. However, Ohnishi *et al.* have shown that obtaining

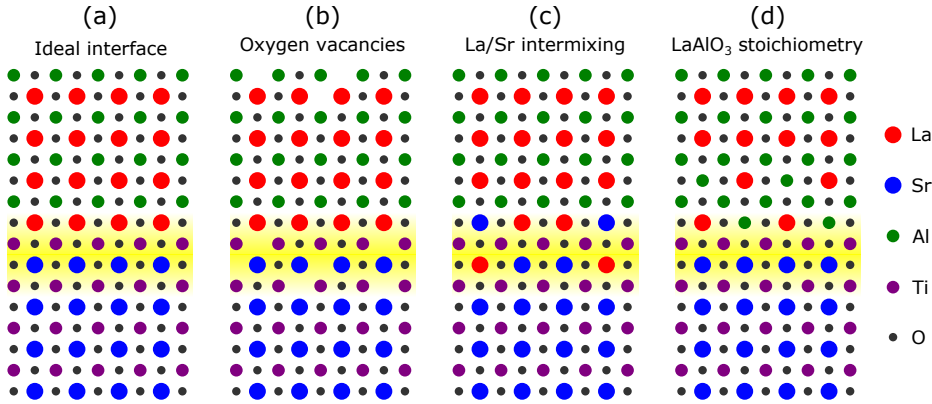


Figure 1.4: (a) An ideal $\text{LaAlO}_3/\text{SrTiO}_3$ interface. (b)-(d) Illustrations of extrinsic defect-driven mechanisms. (b) Oxygen vacancies formed either in SrTiO_3 at the interface or at the LaAlO_3 surface. (c) La/Sr intermixing at the interface. (d) Cation stoichiometry in LaAlO_3 films. Image shows the Al-rich case. The yellow area in each image represent the 2DES.

a stoichiometric film from PLD is a rare case rather than routine [52, 53]. It has been reported by several PLD groups that a slight variation in the growth parameters modifies the cation stoichiometry of LaAlO_3 films, resulting in a dramatic change in the interfacial conductivity [54–56]. The importance of LaAlO_3 stoichiometry has also been addressed by other growth techniques. Dildar *et al.* [57, 58] used on-axis sputtering to grow LaAlO_3 films. In order to prevent backspattering effect, they used high oxygen pressures (typically 1 mbar). The LaAlO_3 films were found to be La-rich ($\text{La}/\text{Al} \approx 1.07$) and the interfaces were insulating. Warusawithana *et al.* [59] used molecular beam epitaxy (MBE). The stoichiometry of the LaAlO_3 films were gradually changed by finely tuning the La and Al fluxes. The interesting outcome is that interfacial conduction can only be observed in Al-rich samples ($\text{La}/\text{Al} \leq 0.97$) as illustrated in Fig. 1.4(d). Their further density functional theory (DFT) calculations showed different roles of defects in the polar catastrophe model. In Al-rich samples, Al can fill La vacancies without changing the net charge of the (001) planes. The electronic reconstruction can still transfer electrons to the interface. In La-rich samples, however, La can not substitute for Al, resulting in the formation of Al_2O_3 -vacancy complexes which prohibits the charge transfer.

1.4. Electrostatic gating of $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures

The main focus of this thesis is electrostatic gating of the $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures. In this section, we first introduce the band structure at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface and then discuss the main geometrical configurations for electrostatic gating and the major experimental observations.

1.4.1. Band structure at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface

SrTiO_3 is a band insulator, where the indirect band gap energy is 3.25 eV and the direct band gap energy is 3.75 eV [60]. The conduction band of SrTiO_3 is dominated by the Ti 3d orbitals, while the valence band is composed of the O 2p orbitals. Fig. 1.5 shows the energy levels of the Ti 3d orbitals in various environments without considering the effect of atomic spin-orbit (SO) coupling. The 3d orbitals (d_{xy} , d_{yz} , d_{xz} , $d_{x^2-y^2}$ and $d_{3z^2-r^2}$) of an isolated Ti atom (spherical symmetry) is five-fold degenerate, which is labeled by the angular momentum $L = 2$. Once the Ti is surrounded by the oxygen octahedron (cubic symmetry, O_h point group), the 3d orbitals are split into a higher-energy doublet (e_g states) and a lower-energy triplet (t_{2g} states). Below 105 K, SrTiO_3 undergoes a ferroelastic transition from cubic to tetragonal symmetry (D_{4h} point group), which slightly shift the d_{xy} state higher in energy relative to the d_{yz} and d_{xz} states. Upon forming the $\text{LaAlO}_3/\text{SrTiO}_3$ interface, the breaking of inversion symmetry further reduces the symmetry of the system to the C_{4v} point group. This does not give rise to additional lifting of degeneracy, but completely modifies the sign and amplitude of the splittings between in-plane and out-of-plane orbitals of the e_g and the t_{2g} states. Salluzzo *et al.* [16, 61] experimentally measured the splitting energies of the e_g and the t_{2g} states to be ~ 100 meV and ~ 50 meV, respectively. The resulting t_{2g} bands are plotted in Fig. 1.5(e). When atomic SO coupling, as shown in Fig. 1.5(f), is taken into account, the combination of broken inversion symmetry and atomic SO coupling gives rise to a more complicated band splitting, as depicted in Fig. 1.5(g), which is responsible for the Rashba effect. This will be discussed further in Chapter 5.

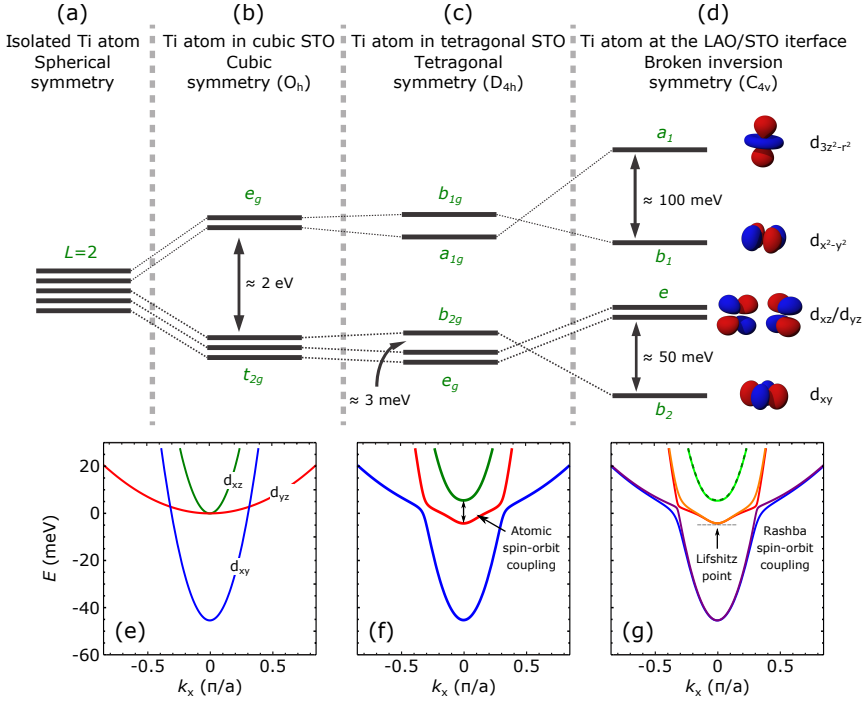


Figure 1.5: Ti electronic level structure at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface. (a) The 3d orbitals of an isolated Ti atom are five-fold degenerate. (b) Once the Ti is surrounded by the oxygen octahedron, the orbitals are split into the e_g states and the t_{2g} states. (c) Below 105 K, SrTiO_3 changes from cubic to tetragonal symmetry, which slightly lifts the orbit degeneracy. (d) Upon forming the $\text{LaAlO}_3/\text{SrTiO}_3$ interface, the breaking of inversion symmetry results in larger splittings of the e_g states and the t_{2g} states. This leads to different d -bands. Images adapted from Ref. [62]. (e)-(g) Effective three-band model at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface. (e) Spin-degenerate t_{2g} bands. (f) The t_{2g} bands with atomic SO coupling included. The three bands are still double degenerate. (g) The t_{2g} bands with atomic SO coupling and inversion asymmetry included. Maximum Rashba spin splitting is at the crossing point of the d_{xy} and $d_{xz,yz}$ orbitals. The Lifshitz point is at the bottom of the $d_{xz,yz}$ bands [63]. Images adapted from Ref. [64].

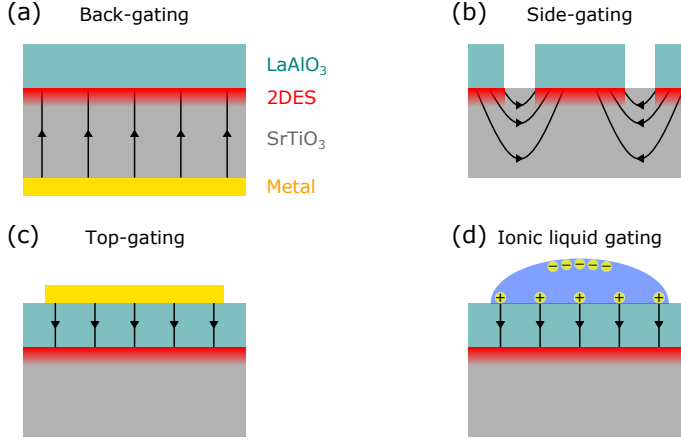


Figure 1.6: Illustrations of different geometrical configurations for $\text{LaAlO}_3/\text{SrTiO}_3$ field-effect devices. (a) Back-gating. (b) Side-gating. (c) Top-gating. (d) Ionic liquid gating. The black lines represent electric field lines induced by an external gate voltage. The legend in (a) applies to all panels.

1.4.2. Electric-field effects in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures

Semiconducting field-effect transistors (FETs) are the workhorses of modern electronics [65]. Thus the capability of controlling the physical properties of novel materials by applying an external electric field is of crucial importance for device applications. A typical semiconductor FET consists of source and drain terminals, a conducting channel between them, and a gate terminal [66, 67]. The channel and gate electrode are separated by an insulating dielectric, forming a parallel plate capacitor. Applying a voltage across this capacitor induces charges into the channel and therefore modulates its conductance.

For the $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures, there are three main geometrical configurations for field-effect devices, namely back-gating [26], side-gating [68], and top-gating [69] as shown in Fig. 1.6(a)-(c). Ionic liquid gating, as shown in Fig. 1.6(d), belongs to the top-gating configuration, but the channel and gate electrode are covered by a drop of ionic liquid, forming an electric double layer [70]. In the past decade, an enormous number of fascinating gate-tunable effects have been achieved at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface by employing different geometries.

Among the possible options, the back-gating geometry is the most widely used one. In this configuration, the gate voltage is applied across the SrTiO_3 substrate. The reported gate-tunable effects include insulator to metal transitions [26], insulator to superconductor transitions [71], Rashba spin-orbit coupling [18, 72–76], Shubnikov – de Haas oscillations [30, 77, 78], and the Lifshitz transition [63]. It should be noted that these effects basically depend on the carrier density, therefore they can be modulated by

other geometries as well.

The side-gating geometry was first developed by the group of J. Levy using conductive atomic force microscopy lithography, which enables an easy writing and erasing of nanoscale structures [68]. Equipped with this technique, they were able to fabricate single-electron transistors [79, 80], control ferromagnetism at room temperature [17], and realize quantized ballistic transport [81] at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface. Recently, Monteiro *et al.* fabricated side-gating devices using electron-beam lithography and realized gate-tunable Josephson junctions [82].

The top-gating geometry works in a similar way as the back-gating counterpart, but the insulating dielectric is the LaAlO_3 overlayer. Compared with back-gating, the big advantage of top-gating is that it requires very low voltages to achieve sizeable gating effects [83–90]. However, the device fabrication process is very complicated which is due to the requirement of multiple aligned lithography steps [91].

Ionic liquid gating is able to achieve a charge transfer that is two orders of magnitude larger than conventional FETs [92]. This technique has been used to induce or modify superconductivity in ZrNCl [93], SrTiO_3 [94], KTaO_3 [95], MoS_2 [96], $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [97], and $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ [98]. It has also been employed to modulate physical properties at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface [70, 99, 100]. Lin *et al.* [70] have observed a gate-tunable Kondo effect and Zeng *et al.* [99] have obtained an electron mobility up to $19380 \text{ cm}^2/\text{Vs}$.

1.5. Outline of this thesis

This thesis is concerned with the fabrication of conducting interfaces made by sputter – growing thin layers of LaAlO_3 on SrTiO_3 , and with studying their magnetotransport properties under the influence of an electric field. The thesis is structured as follows:

- **Chapter 2** provides detailed information of the experimental setups. We start with an introduction to sputter deposition, which is followed by a description of the 90° off-axis sputtering system. Then, we introduce the sample fabrication process, including substrate preparation, thin film deposition, and Hall bar device fabrication. Finally, we discuss the sample characterization techniques, such as atomic force microscopy, x-ray diffraction, and magnetotransport measurements.

- **Chapter 3** presents the growth of high quality epitaxial LaAlO_3 films on SrTiO_3 (001) substrates by 90° off-axis sputtering. First we show the optimization of the growth parameters. Then we demonstrate the tuning of interfacial conductance in $\text{LaAlO}_3/\text{SrTiO}_3$ by varying the sputtering pressure.

- **Chapter 4** focuses on the electron trapping effect in back-gated $\text{LaAlO}_3/\text{SrTiO}_3$. By combining magnetotransport measurements and self-consistent Schrödinger-Poisson calculations, we identify the relation between the amount of trapped electrons and the

gate voltage as well as the spatial distribution of the trapped electrons. We demonstrate that an earlier proposed thermal escape mechanism provides a misleading physical picture, and we propose a new mechanism.

- **Chapter 5** demonstrates the tuning of Rashba spin-orbit coupling in back-gated $\text{LaAlO}_3/\text{SrTiO}_3$. We aim to clarify the inconsistent dependence of Rashba effect on gate voltage in experiments, and examine the theoretical predictions. We trigger the Lifshitz transition multiple times by carefully tuning the gate voltage. By analyzing the weak antilocalization effect of the magnetoresistance, we show that the maximum Rashba effect occurs when the Fermi energy is near the Lifshitz point.

- **Chapter 6** studies the effect of LaAlO_3 thickness on the transport properties in $\text{LaAlO}_3/\text{SrTiO}_3$ when using ionic liquid gating. We demonstrate that the physical properties at the interface are dominated by the intrinsic interactions rather than the LaAlO_3 thickness. We present a Kondo effect, which is enhanced while increasing the gate voltage. We also show a gate-tunable and temperature-dependent anomalous Hall effect, which always emerges near the Kondo temperature.

- **Appendix A** provides a step-by-step description of the self-consistent Schrödinger-Poisson calculations performed for Chapter 4.

2

Experimental setups

2.1. Thin film deposition

In the past few decades, progress in thin film deposition techniques has enabled material growth with unit cell precision, which has led to a large number of breakthroughs. Thin film deposition technologies are generally classified into two categories: physical vapor deposition (PVD) and chemical vapor deposition (CVD) [101]. The $\text{LaAlO}_3/\text{SrTiO}_3$ interface is most commonly formed by pulsed laser deposition (PLD, PVD) [9], while several other growth methods, such as molecular beam epitaxy (MBE, PVD) [59], atomic layer deposition (ALD, CVD) [102] and sputtering (PVD) [57, 103], have also been employed. These alternative methods have not only demonstrated a successful growth of epitaxial $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures, but also provide important experimental evidence for the emergence of interfacial conduction. A famous example is that Al-excess LaAlO_3 films are necessary for forming conductive interfaces as could be demonstrated by MBE [59]. From an application point of view, amongst these methods, sputtering is the most extensively used technique in semiconductor industry. Therefore, fabricating $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures by sputtering also facilitates its industrial application. In this thesis, we use a home-made 90° off-axis radio frequency magnetron sputtering system for growing LaAlO_3 films. In this section, we first introduce the principles of sputter deposition and then discuss the main features of the 90° off-axis sputtering system.

2.1.1. Introduction to sputter deposition

The phenomenon of sputtering was discovered by Sir W. R. Grove in 1852 [104]. It was originally called "cathodic disintegration" which referred to the ejection of small particles. In 1913, Sir J. J. Thomson renamed cathodic disintegration to "spluttering" in his influential monograph [105]. In 1923, Kingdon and Langmuir removed the letter "l" from spluttering in their publication [106]. Ever since, the term "sputtering" has been used to describe cathodic disintegration of materials. The fundamentals of sputtering was already understood in early 20th century. However, sputtering actually played an important role in microelectronic industry since 1970s, because of the progress in sputtering source and vacuum technology.

Sputter deposition can be easily understood by considering a simple DC diode sputtering system, which consists of a cathode and an anode inside a vacuum chamber, as shown in Fig. 2.1(a). The cathode is the sputtering target and the substrate is placed on the anode, which is often at ground potential together with the vacuum chamber. After pumping the chamber to a base pressure (typically 1×10^{-6} mbar), a sputtering gas (usually Ar) is introduced into the chamber, reaching a pressure between 1×10^{-3} to 1×10^{-1} mbar. With a sufficient DC voltage applied between the electrodes, the gas will breakdown to form a plasma. The positively charged Ar^+ ions are accelerated to-

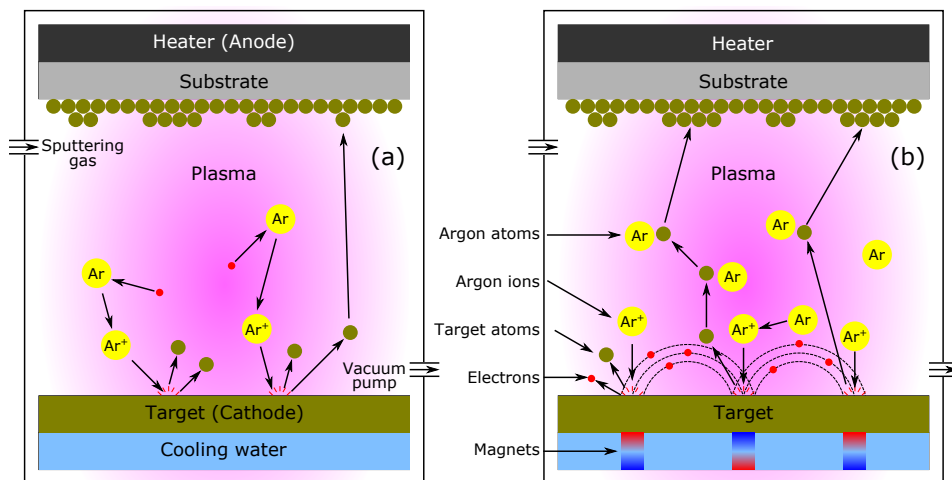


Figure 2.1: Principles of sputter deposition. (a) In a DC diode sputtering system, Ar atoms are ionized by a strong electric potential difference, and these ions are accelerated to the target. After impact, target atoms are released and travel to the substrate, where they form a thin film of the target material. (b) In a magnetron sputtering system, the electrons are confined near the target surface, which results in greater Ar ion replenishment and less damage of the substrate.

wards the negatively charged target to eject atoms from its surface. The ejected atoms then travel to the substrate and finally condense onto the substrate to form a thin film of the target material. DC sputtering can be operated only if the target is conductive. If the target is insulating, positive charges will build up at the target surface and repels the incident Ar^+ ions. Consequently, the negative voltage on the target becomes lower than the breakdown voltage required to sustain the discharge.

The problem can be overcome by coupling a radio frequency (RF) voltage capacitively to the insulating target and the plasma. The commonly used frequency is 13.56 MHz. The electrons in the plasma oscillate with this high-frequency electric field, which results in two important effects. First, the positive surface charges are neutralized by the electrons in each RF cycle. Second, the electrons gain enough energy to make ionizing collisions to sustain the discharge. In contrast, the massive Ar^+ ions in the plasma have too much inertia to follow 13.56 MHz and can only respond to the time-averaged electric field, which makes that the target self-biases to a negative potential. This bias, called DC bias, is generally related to the energy of the Ar^+ ions hitting the target. In practice, an impedance matching network is required in order to transfer the RF power into the system more efficiently. The matching networks usually consist of capacitors and inductors. There are many different designs in the market but their sole purpose is to convert the impedance of the chamber to $50\ \Omega$.

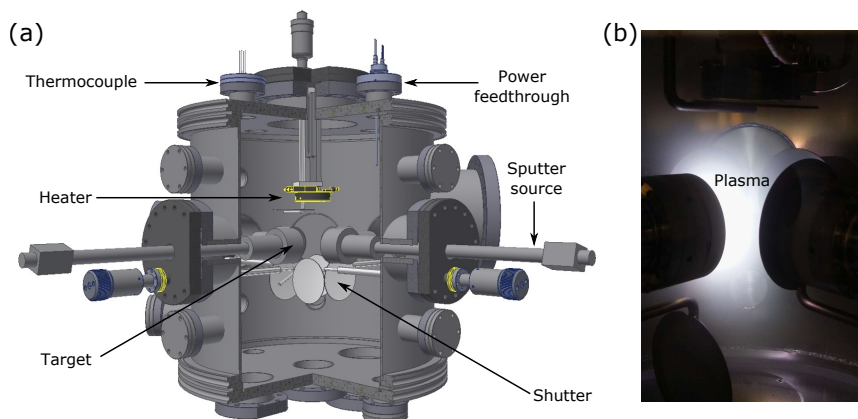


Figure 2.2: (a) A sketch of the 90° off-axis sputtering system. Image plotted by F. Schenkel. (b) A photo of the chamber taken during sputtering. The bright area is the plasma.

A common way to enhance the sputtering process is to use a magnetron sputtering source as shown in Fig. 2.1(b). The strong magnetic fields guide electrons to spiral along the magnetic flux lines near the target surface instead of being attracted toward the substrate. The enhanced confinement of electrons has two advantages. First, electrons travel for longer distances, increasing the probability of ionizing Ar atoms. Second, it prevents damages to the film caused by bombardment from the electrons.

2.1.2. 90° off-axis sputtering

Conventional sputter deposition uses the on-axis geometry, where the substrate faces the target directly. However, when growing oxide films, backsputtering of the substrate by high-energy particles (O^- and sputtered atoms) usually degrades the quality of films. The problem can be solved by changing the relative position between the substrate and the target. The 90° off-axis geometry, where the substrate and the target are at a right angle, was first employed by Eom *et al.* [107, 108] for growing $YBa_2Cu_3O_7$ thin films. This technique benefits both from off-axis geometry and high sputtering pressure. The idea is that the off-axis geometry places the substrate outside the plasma, and the sputtered atoms experience many scattering events with the sputtering gas to slow down before landing on the substrate. As a consequence, bombardments from high-energy particles are largely minimized.

A sketch of the 90° off-axis sputtering system in Leiden is shown in Figure 2.2(a). It is based on a system in use in the group of J.-M. Triscone in Geneva, who readily provided the technical details. A resistive heater (Twente Solid State Technology) is fixed on the central holder, and is grounded to the chamber. Four 2-inch magnetron sputtering

sources (MeiVac) are installed to the chamber wall at angles of 90° . Sputtering targets are glued to copper plates by epoxy adhesive silver. Magnetic keepers are screwed to the back of the copper plates and the targets are attached to the central magnet on the sputtering sources. The working distances are set at 75 mm from the surface of the heater to the axis of the target and 45 mm from the surface of the target to the axis of the heater. It should be noted that the working distances strongly affect the optimal growth parameters, especially the sputtering pressure. Three gas lines, namely Ar, O_2 and N_2 (Linde gas, purity $\geq 99.999\%$), are connected to the chamber and the gas flows are measured by mass flow controllers (Brooks Instrument). The system is turbo-pumped and reaches a base pressure of 1×10^{-7} mbar. During sputtering, the chamber pressure is controlled by a butterfly valve (VAT) and the RF power is delivered to the sputtering source by Advanced Energy power supply (RFX-600) and matching networks (ATX-600). A photo of the chamber during sputtering is shown in Figure 2.2(b), where the heater is positioned well outside of the plasma.

2.2. Sample fabrication

2.2.1. Substrate Preparation

It was demonstrated in the original paper by Ohtomo and Hwang that a conductive interface can only be formed by growing $LaAlO_3$ on TiO_2 -terminated $SrTiO_3$ [9]. The first step of our sample fabrication process is substrate preparation. The single crystalline $SrTiO_3$ substrates used in this thesis are ordered from CrysTec GmbH. They are (001) oriented with dimensions of $5 \times 5 \times 0.5 \text{ mm}^3$ and miscut angles of 0.1° - 0.3° .

The as-received substrate usually has a mixed surface termination of SrO and TiO_2 . We follow the recipe established by Koster *et al.* [109] to obtain a pure TiO_2 termination. The substrate is first ultrasonically cleaned in acetone, ethanol and isopropanol for 10 min, respectively, to remove dust. It is then soaked in millipore water ($18.2 \text{ M}\Omega \text{ cm}$ at 25°C) in an ultrasonic bath for 30 min. This is an important step, during which the SrO -terminated areas form a Sr -hydroxide complex which is known to be dissolvable in acid, while the chemically stable TiO_2 -terminated areas remain unaffected. To dissolve the Sr -hydroxide complex the substrate is etched in buffered HF ($NH_4F:HF = 7:1$, J. T. Baker) for 30 s. Finally, it is annealed in a quartz tube placed in a tube furnace (Lindberg/Blue) at 980°C for 1 h with an oxygen flow of 150 sccm to remove the residuals of the previous treatments and facilitate recrystallization.

Fig. 2.3(a) shows a typical atomic force microscopy image of a TiO_2 -terminated $SrTiO_3$ substrate. An atomically flat surface with step-and-terrace structures can be clearly seen. As shown in Fig. 2.3(b), the step height corresponds to the $SrTiO_3$ (001) interplanar distance ($\sim 3.91 \text{ \AA}$) and the terrace width is about 200 nm.

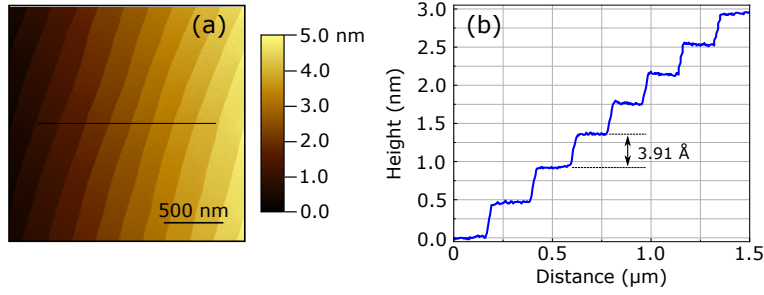


Figure 2.3: (a) A typical atomic force microscopy image of TiO_2 -terminated SrTiO_3 substrate. (b) A step-and-terrace profile. The step height is $\sim 3.91 \text{ \AA}$ and the terrace width is about 200 nm.

2.2.2. Thin film growth

The substrate is first glued on the heater by uniformly applying a thin layer of silver paste (SPI Supplies) to the unpolished side. In order to get a good thermal contact and adhesion with the heater, the substrate is then baked at 200°C for 1 h in the chamber. Before deposition the chamber is usually pumped overnight.

When growing a film, the substrate is first heated up to the growth temperature at a rate of $25^\circ\text{C}/\text{min}$. Ar is then introduced into the chamber as the sputtering gas. Next, the target is pre-sputtered for at least 15 min while keeping the substrate shutter closed. After pre-sputtering, the deposition is started by opening the substrate shutter. The film thickness is controlled by varying the sputtering time. Since the film is grown in a reducing atmosphere, a post oxygen annealing treatment is necessary to remove the oxygen vacancies formed in the substrate. After deposition, the sample is cooled down to 600°C at a rate of $10^\circ\text{C}/\text{min}$, while the sputtering gas is pumped out at the same time. When the temperature stabilizes, oxygen is introduced into the chamber, reaching a pressure of 1 mbar. The annealing time is 1 h. After oxygen annealing, the sample is cooled down to room temperature in the same oxygen atmosphere and at the same cooling rate. The above steps describe the general film growth procedure. The optimization of growth parameters is discussed in more detail in Chapter 3.

2.2.3. Hall bar device fabrication

Besides unpatterned films, we also fabricated Hall bar devices using photolithography for electrostatic gating experiments. We use a Karl Suss Mask Aligner equipped with a 365 nm (i-line) ultraviolet (UV) lamp. A self-designed 5-inch chrome mask plate is ordered from Delta Mask, which contains Hall bar structures with different dimensions. The photoresist (OiR 907-12) and developer (OPD 4262) are from Fujifilm. A schematic of the device fabrication process is shown in Fig. 2.4.

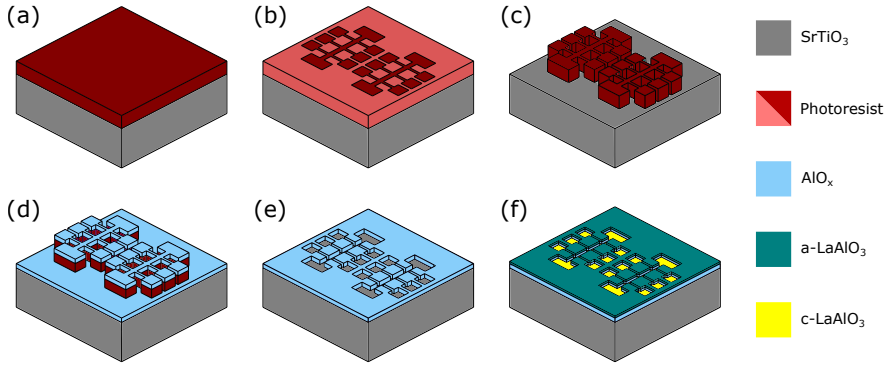


Figure 2.4: A schematic of the Hall bar device fabrication process. (a) Spin coating. (b) UV light exposure. (c) Photoresist development. (d) AlO_x film deposition. (e) Lift-off. (f) LaAlO_3 film deposition.

First (Fig. 2.4(a)), the photoresist is spin coated (4000 rpm) on a TiO_2 -terminated SrTiO_3 substrate. The sample is then baked on a hot plate at 80°C for 1 min.

Second (Fig. 2.4(b)), the sample is exposed in UV light for 6 s. OiR 907-12 is a positive resist, therefore we cover the Hall bar pattern and expose the rest area.

Third (Fig. 2.4(c)), the sample is developed in OPD 4262 for 1 min, followed by dipping in a stop bath (millipore water) for 1 min. A Hall bar structure made of photoresist is now formed on the substrate.

Fourth (Fig. 2.4(d)), an amorphous AlO_x layer (~ 15 nm) is sputtered (DC bias set to -750 V) on the sample by a Leybold-Heraeus sputtering system. In order to prevent hardening of the photoresist, we alternate the sputtering on and off in every 1 min, which is achieved by rotating the sputtering source back and forth with a motor.

Fifth (Fig. 2.4(e)), the sample is soaked in acetone overnight to lift-off the photoresist. The sample is then ultrasonicated in acetone and isopropanol, both for 5 min. The substrate is now covered by an AlO_x hard mask except for the Hall bar pattern.

Finally (Fig. 2.4(f)), the LaAlO_3 film is grown by the process mentioned above. The LaAlO_3 layer formed on the Hall bar pattern is crystalline and conductive while the layer formed on AlO_x is amorphous and insulating.

It is worth mentioning that after step 5, there is usually some residual photoresist left on the Hall bar pattern as shown in Fig. 2.5(a). The problem cannot be solved by lowering the DC bias or extending the soaking time in acetone. However, the residual photoresist can be cleaned away during heating up the substrate to the growth temperature as shown in Fig. 2.5(b). We have also tried to fabricate Hall bar devices in the same procedure but using e-beam lithography (PMMA from Allresist). However, we usually find more residual resist on the Hall bar pattern, which cannot be removed by heating up the substrate to high temperatures.

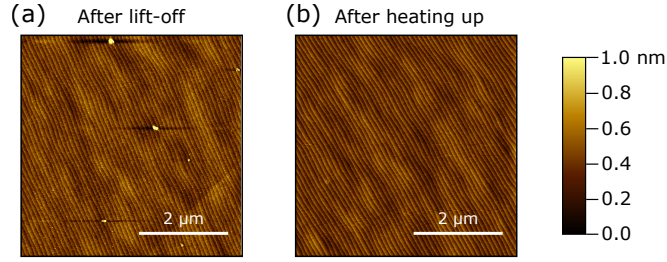


Figure 2.5: (a) An AFM image of the Hall bar channel after lift-off. Residual photoresist is clearly visible. (b) An AFM image taken after heating up the substrate to 800 °C. Residual resist is cleaned away during the heating up process.

2.3. Sample characterization

The main disadvantage of our sputtering system is that it lacks *in situ* tools such as reflection high-energy electron diffraction (RHEED) or a quartz crystal monitor to check the growth process. Therefore, we rely on *ex situ* characterization techniques, such as atomic force microscopy and x-ray diffraction, to determine the thickness and lattice constants of the LaAlO_3 films.

2.3.1. Atomic force microscopy

Atomic force microscopy (AFM) is a type of scanning probe microscopy (SPM), which was invented by Binnig *et al.* [110] in 1986. It is one of the foremost techniques for characterizing surface topography with nanometer resolution. AFM is based on measuring the repulsive and attractive forces between atoms on the probe and those on the sample surface. Therefore it enables measurements on insulating materials. An AFM basically consists of a laser, a four-sectional photodiode and a piezoelectric scanner. In the measurement, a spring microcantilever with a sharp tip (typical radius less than 10 nm) scans over the sample surface in a raster-like pattern. As the tip interacts with the sample surface, the laser spot is reflected from the cantilever and detected by the photodiode. In order to maintain feedback parameters constant, a feedback loop uses the laser deflection to adjust the height of the cantilever, forming the surface topology. We use a Bruker AFM and choose its tapping mode, where the topology is mapped by an oscillating tip lightly tapping the sample surface.

2.3.2. X-ray diffraction

High resolution x-ray diffraction (HRXRD) is a powerful tool for nondestructive investigations of thin films, heterostructures and superlattices. The high resolution is achieved by using combinations of high quality mirror and monochromator. We use a Bruker XRD

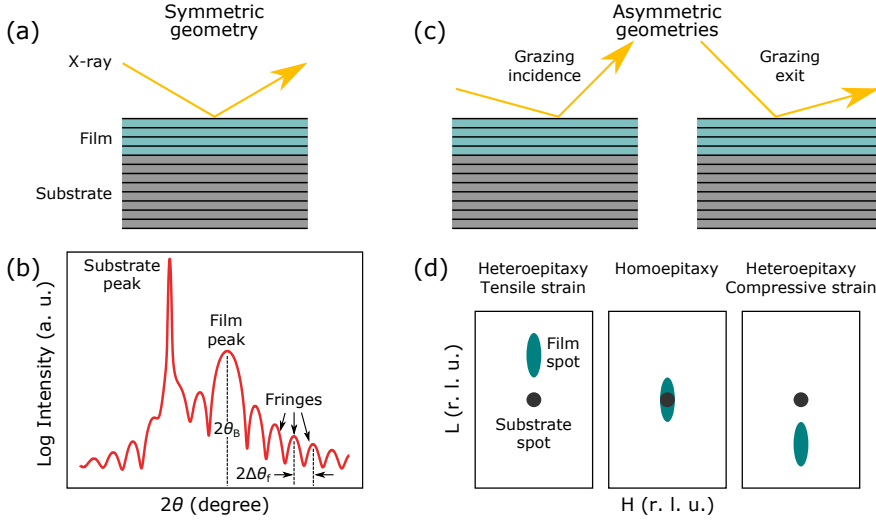


Figure 2.6: Schematics of high resolution x-ray diffraction. (a) A sketch of the symmetric geometry. (b) A canonical result of a θ - 2θ scan. The film peak appears at $2\theta_B$ and the difference between interference fringes is $2\Delta\theta_f$. Image adapted from open source. (c) Sketches of the asymmetric geometries. (d) Canonical results of reciprocal space mapping. The map is in reciprocal lattice units (r. l. u.) based on the principal Bragg indices H , K and L . In the geometry used, $(H0L)$ spots are measured. The relative position between the substrate spot (black) and film spot (teal) depends on the epitaxial strain on the film.

(D8 DISCOVER) which is equipped with a Cu $K_{\alpha 1}$ ($\lambda = 1.541 \text{ \AA}$) monochromator in the incident beam optics and a motorized receiving slit in the diffracted beam optics. This equipment was kindly made available by A. Caviglia at Delft University of Technology. The routine measurements include θ - 2θ scans and reciprocal space mapping, which allow for the precise measurement of film thickness and lattice constants.

The θ - 2θ scan is performed in a symmetric geometry as shown in Fig. 2.6(a). A canonical result is plotted in Fig. 2.6(b). The film peak appears at $2\theta_B$. The lattice constant perpendicular to the surface, d (also called the out-of-plane lattice constant), can be obtained from the Bragg equation,

$$2d \sin \theta_B = n\lambda, \quad (2.1)$$

where n (integers) is the diffraction order and λ is the x-ray wavelength. Moreover, interference fringes are usually observed next to the main diffraction peak. The angular difference between such secondary maxima, $\Delta\theta_f$, can be used to determine the film thickness [111],

$$t = \frac{\lambda}{2\Delta\theta_f \cos \theta_B}, \quad (2.2)$$

where $\Delta\theta_f$ is in rad.

Reciprocal space mapping (RSM) is performed in an asymmetric geometry, which allows for the determination of both the in-plane (a_{film}) and out-of-plane (c_{film}) lattice constants. There are two asymmetric geometries, namely grazing incidence (GI) and grazing exit (GE) as shown in Fig. 2.6(c). We use the GI geometry, since it is more surface sensitive compared with the GE geometry. It is known that a lattice plane in real space corresponds to a point in reciprocal space. Typical RSM results around the ($H0L$) diffraction peak are plotted in Fig. 2.6(d). The black and teal spots represent the substrate and film peaks, respectively. The elongation of the film spot is due to finite thickness effects. In all of the three cases, the film is fully strained to the substrate, with equal values of H for both. However, the relative position between the substrate and film spots for the out-of-plane component depends on the epitaxial strain on the film through the Poisson's ratio which is a measure of the Poisson effect. The Poisson effect is a phenomenon in which a material tends to contract in the directions perpendicular to the direction of stretching, and vice versa. When $a_{\text{film}} = a_{\text{sub}}$, the substrate and film spots overlap with each other. When $a_{\text{film}} < a_{\text{sub}}$ ($a_{\text{film}} > a_{\text{sub}}$), the film experiences a tensile (compressive) strain from the substrate. The film spot will appear above (below) the substrate spot. The lattice constants can be calculated by

$$\frac{a_{\text{sub}} - a_{\text{film}}}{a_{\text{sub}}} = \frac{\Delta H}{H} \quad \text{and} \quad \frac{c_{\text{sub}} - c_{\text{film}}}{c_{\text{sub}}} = \frac{\Delta L}{L} \quad (2.3)$$

2.3.3. Magnetotransport measurements

Magnetotransport properties of the $\text{LaAlO}_3/\text{SrTiO}_3$ interface are the main focus of this thesis. Two cryostats are used for the measurements. One is a Quantum Design Physical Property Measurement System (PPMS), which controls magnetic fields up to 9 T and temperatures ranging from 1.9 K to 400 K. The other cryostat is in the high field magnet laboratory (HFML) of Radboud University Nijmegen, which is equipped with a 15 T superconducting magnet. Two temperatures can be easily stabilized in the Nijmegen cryostat, namely 4.2 K (pump valve fully closed) and 1.2 K (pump valve fully open).

Van der Pauw method

We use the van der Pauw method to measure unpatterned samples. This method was suggested by L. J. van der Pauw in 1958 [112, 113]. As shown in Fig. 2.7(a), four ohmic contacts 1, 2, 3, and 4 are formed at the corners by wedge bonding aluminum wire directly to the sample surface. We also make four scratches using a diamond knife to minimize errors arising due to the finite extent of contacts.

To measure the sheet resistance R_s (also called the longitudinal resistance R_{xx}), a current is applied along one edge (for example, I_{12}) of the sample and the voltage across the opposite edge (in this case, V_{43}) is measured. The resistance along the vertical edge,

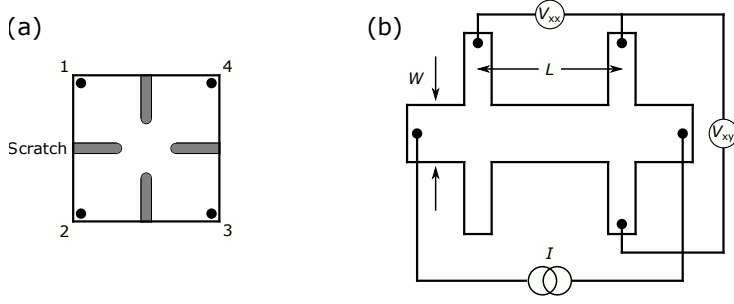


Figure 2.7: Sample geometries for magnetotransport measurement. (a) Van der Pauw method. (b) Hall bar geometry.

$R_{12,43}$, can be obtained using Ohm's law, $R_{12,43} = V_{43}/I_{12}$. In a similar way, we can obtain a resistance along the horizontal edge, such as $R_{23,14}$. These two resistances are related to R_s by the van der Pauw formula

$$e^{\frac{-\pi R_{12,43}}{R_s}} + e^{\frac{-\pi R_{23,14}}{R_s}} = 1. \quad (2.4)$$

In practice, a more accurate measurement can be performed by exchanging the current source and voltage meter as well as switching their polarities. The vertical and horizontal resistances are then given by

$$R_v = \frac{R_{12,43} + R_{21,34} + R_{34,21} + R_{43,12}}{4} \quad \text{and} \quad R_h = \frac{R_{23,14} + R_{32,41} + R_{14,23} + R_{41,32}}{4}. \quad (2.5)$$

We use a fast-converging Newton-Raphson method to obtain R_s , where the next approximation R_s^+ is calculated by

$$R_s^+ = R_s + R_s^2 \frac{1 - e^{\frac{-\pi R_v}{R_s}} - e^{\frac{-\pi R_h}{R_s}}}{\pi(R_v e^{\frac{-\pi R_v}{R_s}} + R_h e^{\frac{-\pi R_h}{R_s}})}. \quad (2.6)$$

The calculation converges when $(R_s^+ - R_s)/R_s$ is less than the tolerable error (0.01 % in our calculation).

To measure the Hall resistance R_{Hall} (also called the transverse resistance R_{xy}), a magnetic field is applied normal to the sample surface. The applied current, the measured voltage and the magnetic field must be perpendicular to each other. For instance, a current is driven from 1 to 3, and the voltage between 2 and 4 is measured. Two sets of measurements need to be made: one with the magnetic field in the positive (P) z -direction and the other in the negative (N) z -direction. Combining all the measurement configurations, R_{Hall} is given by

$$R_{\text{Hall}} = \frac{(R_{13,24,P} - R_{13,24,N}) + (R_{31,42,P} - R_{31,42,N}) + (R_{24,31,P} - R_{24,31,N}) + (R_{42,13,P} - R_{42,13,N})}{8}. \quad (2.7)$$

Hall bar geometry

For a Hall bar geometry as shown in Fig. 2.7(b), the measurement and calculation are much easier. An electrical current, I , is applied along the Hall bar channel. The longitudinal voltage, V_{xx} , and transverse voltage, V_{xy} , can be measured simultaneously. The sheet resistance is given by

$$R_s = \frac{V_{xx}}{I} \frac{W}{L}, \quad (2.8)$$

where W is the Hall bar width and L is the distance between two voltage probes. The Hall resistance is given by

$$R_{\text{Hall}} = \frac{V_{xy}}{I}. \quad (2.9)$$

Determination of carrier density and mobility

The carrier density (n_s) and mobility (μ) of the sample are determined from magnetotransport measurements. It is well known that the 2DES at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface changes from one-band conduction to two-band conduction after a Lifshitz transition [63], which corresponds to the Hall resistance changing from linear to nonlinear¹.

In the one-band regime, n_s and μ are given by [115]

$$n_s = \frac{B}{eR_{\text{Hall}}} \quad \text{and} \quad \mu = \frac{R_{\text{Hall}}}{BR_s(B=0)}, \quad (2.10)$$

where e is the electron charge and B is the magnetic field.

In the two-band regime, the carrier densities and mobilities can be extracted by fitting the magnetotransport data with a two-band model [115]

$$R_s = \frac{1}{e} \cdot \frac{\frac{n_1\mu_1}{1+(\mu_1B)^2} + \frac{n_2\mu_2}{1+(\mu_2B)^2}}{\left(\frac{n_1\mu_1}{1+(\mu_1B)^2} + \frac{n_2\mu_2}{1+(\mu_2B)^2}\right)^2 + \left(\frac{n_1\mu_1^2B}{1+(\mu_1B)^2} + \frac{n_2\mu_2^2B}{1+(\mu_2B)^2}\right)^2} \quad (2.11)$$

and

$$R_{\text{Hall}} = \frac{1}{e} \cdot \frac{\frac{n_1\mu_1^2B}{1+(\mu_1B)^2} + \frac{n_2\mu_2^2B}{1+(\mu_2B)^2}}{\left(\frac{n_1\mu_1}{1+(\mu_1B)^2} + \frac{n_2\mu_2}{1+(\mu_2B)^2}\right)^2 + \left(\frac{n_1\mu_1^2B}{1+(\mu_1B)^2} + \frac{n_2\mu_2^2B}{1+(\mu_2B)^2}\right)^2}, \quad (2.12)$$

where $n_{1(2)}$ and $\mu_{1(2)}$ are the carrier density and mobility of the first (second) band, respectively.

¹It should be noted that a nonlinear Hall resistance can also arise due to anomalous Hall effect [114].

3

Controlling the interfacial conductance in $\text{LaAlO}_3/\text{SrTiO}_3$ in 90° off-axis sputter deposition

In this Chapter, we mainly study the fabrication of conducting interfaces between LaAlO_3 and SrTiO_3 by 90° off-axis sputtering in an Ar atmosphere. At a growth pressure of 0.04 mbar the interface is metallic, with a carrier density of the order of $1 \times 10^{13} \text{ cm}^{-2}$ at 3 K. By increasing the growth pressure, we observe an increase of the out-of-plane lattice constants of the LaAlO_3 films while the in-plane lattice constants do not change. Also, the low-temperature sheet resistance increases with increasing growth pressure, leading to an insulating interface when the growth pressure reaches 0.10 mbar. We attribute the structural variations to an increase of the La/Al ratio, which also explains the transition from metallic behavior to insulating behavior of the interfaces. Our research shows that the control which is furnished by the Ar pressure makes sputtering as versatile a process as pulsed laser deposition, and emphasizes the key role of the cation stoichiometry of LaAlO_3 in the formation of the conducting interface.

Parts of this Chapter have been published as C. Yin, D. Krishnan, N. Gauquelin, J. Verbeeck, and J. Aarts, *Controlling the interfacial conductance in $\text{LaAlO}_3/\text{SrTiO}_3$ in 90° off-axis sputter deposition*, Physical Review Materials **3**, 034002 (2019) [116].

3.1. Introduction

The discovery of a high-mobility conductive interface between LaAlO_3 and SrTiO_3 has given rise to numerous investigations since 2004 [9]. This two-dimensional electron system (2DES) exhibits many intriguing physical properties, including superconductivity [6], signatures of magnetism [7, 10–12, 15], and multiple electric field tunable effects [18, 26, 30, 63, 71, 72]. However, after 15 years of intensive study, the origin of the 2DES is still under debate. Proposed explanations basically fall into two classes, namely intrinsic charge transfer and extrinsic defects mechanisms. The intrinsic mechanism considers polar discontinuity between the polar LaAlO_3 and the nonpolar SrTiO_3 , which leads to a charge transfer above a critical thickness of LaAlO_3 films [23]. The extrinsic mechanisms involve defects formed at the interface during the film deposition process, such as oxygen vacancies in the SrTiO_3 substrate [41–43] and cation intermixing at the interface [32, 50].

Pulsed laser deposition (PLD) is by far the most commonly used growth method to prepare $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces. During the PLD process, high-energy particle bombardments could introduce the above defects at the interface, which makes it difficult to understand the roles of the intrinsic and extrinsic mechanisms [32].

Alternative growth techniques bring new insights here. Warusawithana *et al.* [59] have grown LaAlO_3 films by molecular beam epitaxy (MBE). The interesting outcome is that interfacial conductance can only be observed in Al-rich samples ($\text{La}/\text{Al} \leq 0.97$). Their further density functional theory (DFT) calculations demonstrate the different roles of defects in the charge transfer mechanism. In Al-rich samples, Al can fill La vacancies without changing the net charge of the (001) planes. The electronic reconstruction can still transfer electrons to the interface. In La-rich samples, however, La can not substitute for Al, resulting in the formation of Al_2O_3 -vacancy complexes which prohibits the charge transfer.

Sputter deposition has also been used. High-pressure (typically 1 mbar) on axis sputtering in pure oxygen yielded LaAlO_3 films with a La/Al ratio of 1.07, and insulating interfaces [57]. Podkaminer *et al.* [103] have shown that 90° off-axis sputtering in pure Ar is capable of growing epitaxial and smooth LaAlO_3 films with conductive interfaces.

In this Chapter, we first show the optimization of growth parameters for depositing high quality epitaxial LaAlO_3 films by 90° off-axis sputtering. We use Ar as sputter gas but we also investigate the effect of mixing in oxygen. Then we demonstrate the tuning of La/Al ratio in LaAlO_3 films by varying sputtering pressures. As a consequence, we observe strong but controlled variations in the interfacial conductivity.

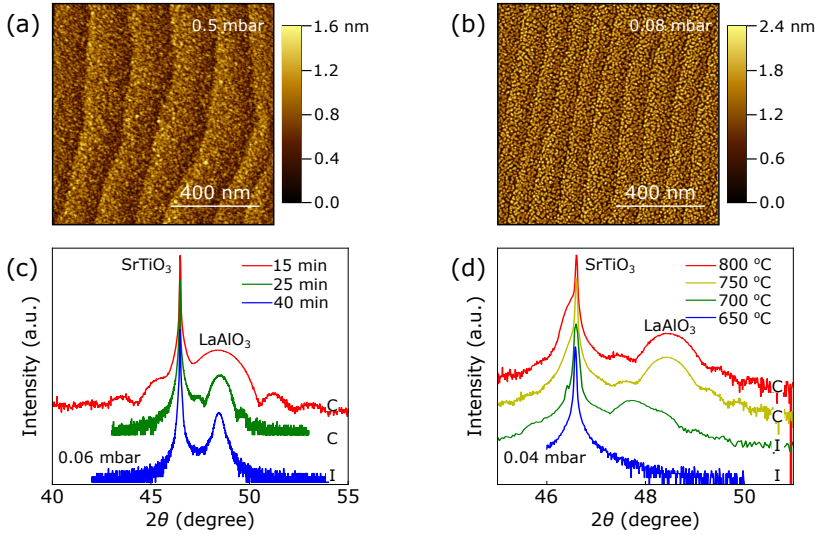


Figure 3.1: Optimization of growth parameters. (a) AFM image of a insulating sample grown by a sintered LaAlO_3 target. The sample was grown at 800°C and 0.5 mbar. A single crystal LaAlO_3 wafer was later used as the sputtering target. (b) AFM image of an insulating sample grown in a mixture of Ar and O_2 . The sample was grown at 800°C with a total pressure of 0.08 mbar and an O_2 partial pressure of 2.0×10^{-3} mbar. (c) The θ - 2θ scans for samples grown at 800°C and 0.06 mbar for various times. "C" and "I" represent conductive and insulating, respectively. (d) The θ - 2θ scans for samples grown at various temperatures and 0.06 mbar for 25 min.

3.2. Optimization of growth parameters

The main control parameters for sputter deposition include RF power, growth temperature and sputtering pressure. In Ref. [103], Podkaminer and co-workers used a single crystal LaAlO_3 wafer as the sputtering target. Conductive $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces were prepared at a RF power of 50 W, a growth temperature of 780°C and an Ar pressure of 0.27 mbar. Before deposition, the target was pre-sputtered for at least 15 min to stabilize a background oxygen partial pressure produced from the target. After deposition, the samples were annealed for 1 h in 400 mbar O_2 at 600°C to remove oxygen vacancies formed in the SrTiO_3 substrates. In our experiments, we follow this procedure and keep the RF power constant at 50 W. In this section, we show the roles of different growth parameters in the formation of conductive interfaces.

Sputtering target

We first used a 2-inch commercial LaAlO_3 target (99.9 %, K. J. Lesker), which was fabricated by sintering. The growth temperature and Ar pressure were 800°C and 0.27 mbar, respectively. The sample surface was very rough and the interface was insulating. The

surface roughness was greatly reduced by increasing the Ar pressure. Fig. 3.1(a) shows the AFM image of a sample grown at 0.5 mbar, however the interface was still insulating. There are two problems in using a sintered target. First, the DC bias on the target is relatively high (typically ~ -175 V). The ejected high-energy atoms still cause a severe back sputtering at lower Ar pressures. Although the surface morphology can be improved by increasing the Ar pressure, the enhanced scattering of light Al atoms may result in La-rich films [54, 57]. Second, the sintered target probably produces too much atomic oxygen during sputtering, which is due to that oxygen diffuses out along grain boundaries. Therefore, we later changed to a 2-inch single crystal LaAlO_3 wafer (MTI Corporation) as the sputtering target. The DC bias was effectively lowered (typically ~ -85 V) and conductive $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces could be formed at a growth temperature of 800°C and Ar pressures ranging from 0.04 to 0.08 mbar.

Oxygen in sputtering gas

Podkaminer *et al.* [103] have obtained insulating $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces using a mixed sputtering gas ($\text{O}_2:\text{Ar} = 3:4$). We tried to mix Ar with a much smaller amount of O_2 , ranging from 0.3 % to 4.2 %. The corresponding oxygen partial pressures (P_{O_2}) are between 1.6×10^{-4} and 4.5×10^{-3} mbar, which are similar to the typical growth pressures used in PLD [10]. However, we observed grainy surfaces and insulating interfaces in all of the samples. Detailed information can be found in Ref. [117]. Fig. 3.1(b) shows the AFM image of a sample grown at 800°C with a total pressure of 0.08 mbar and a P_{O_2} of 2.0×10^{-3} mbar. We conclude that conductive $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces can only be obtained by growing LaAlO_3 films in pure Ar.

Post oxygen annealing

Since the samples are grown in a reducing atmosphere, a large amount of oxygen vacancies will form in the SrTiO_3 substrate, making the SrTiO_3 bulk highly conductive [40]. Therefore, *in situ* oxygen annealing is essential to remove the oxygen vacancies in SrTiO_3 . The annealing treatment is usually performed at an O_2 pressure of several hundreds of millibar [45, 46, 103]. However, this is practically impossible due to the limitations of our experimental setup. The chamber volume is ~ 200 L, but the maximum oxygen flow is only 100 sccm. Therefore, it takes several tens of hours to reach the desired pressures. In our experiments, the oxygen annealing is performed at 1 mbar. We prepared two testing samples to check the effectiveness of our annealing treatment. One sample was a bare SrTiO_3 substrate heated up to 800°C without film deposition. The other was an amorphous $\text{LaAlO}_3/\text{SrTiO}_3$ sample grown at room temperature and 0.08 mbar. Both samples were highly conductive, which indicates the presence of oxygen vacancies [36, 40, 45, 46].

The samples were then annealed for 1 h in 1 mbar O₂ at 600 °C and were found to be insulating.

Film thickness

Liu *et al.* [118] have shown that epitaxial strain plays an important role in controlling the conductivity at the LaAlO₃/SrTiO₃ interface. We deposited three samples at 800 °C and 0.06 mbar for various times. The θ -2 θ scans are shown in Fig. 3.1(c). The interference fringes can be observed for the samples grown for 15 min (~ 16 uc) and 25 min (~ 27 uc) and both samples are conductive. For the sample grown for 40 min, the LaAlO₃ diffraction peak shifts slightly to lower angle and the interference fringes are no longer visible, indicating a relaxation of the LaAlO₃ layer. The sample is insulating.

Growth temperature

Caviglia *et al.* [30] fabricated high-mobility samples by depositing LaAlO₃ films at 650 °C in PLD. We sputtered four samples at various temperatures and 0.04 mbar for 25 min. The θ -2 θ scans are shown in Fig. 3.1(d). The LaAlO₃ diffraction peak cannot be observed for the sample grown at 650 °C, while the sample grown at 700 °C shows a broad peak. Both samples are insulating. Clear LaAlO₃ peaks and interference fringes are visible for the samples grown at 750 °C and 800 °C. Both samples are conductive, which indicates that a higher growth temperature is necessary for the crystallization of the LaAlO₃ films.

3.3. Controlling conductivity by varying sputtering pressure

Having optimized the growth parameters, we now focus on the role of sputtering pressure in influencing the conductivity at the LaAlO₃/SrTiO₃ interface. We prepared five samples at 800 °C and various Ar pressures, ranging from 0.04 to 0.10 mbar (see Table 3.1). In the following the samples will be referred to with their growth pressure (sample 004 is grown at 0.04 mbar). Surface topologies were measured by tapping mode AFM. Epitaxial qualities of the interfaces were characterized by scanning transmission electron microscopy (STEM). Film thicknesses and lattice constants were determined by HRXRD. Magnetotransport properties were measured in the PPMS by the van der Pauw method. Ohmic contacts were formed by wedge bonding Al wire directly to the sample surface.

3.3.1. Surface and interface

Fig. 3.2(a)-(e) show the AFM topographic images of the five samples. Atomically flat surfaces with clear step-and-terrace structures can be observed. The insets show the step height which corresponds to the SrTiO₃ (001) interplanar distance (≈ 3.905 Å).

Table 3.1: Growth pressure, in-plane lattice constant (a_{LAO}), out-of-plane lattice constant (c_{LAO}), thickness (t_{LAO}), deposition time, deposition rate and La/Al ratio of LaAlO_3 films. a_{LAO} was determined from the reciprocal space map. c_{LAO} and t_{LAO} were determined by fitting the θ - 2θ scan. The deposition rate was calculated from the film thickness and the deposition time. The La/Al ratio was determined by interpolating c_{LAO} using the published results in Ref. [119].

Growth Pressure (mbar)	a_{LAO} (Å)	c_{LAO} (Å)	t_{LAO} (u.c.)	Dep. time (min)	Dep. rate (Å/min)	La/Al ratio
0.04	3.905(2)	3.734	16	14.0	4.27	0.88
0.06	3.905(1)	3.739	15	14.0	4.01	0.89
0.08	3.905(1)	3.745	15	14.8	3.79	0.91
0.09	3.905(2)	3.751	14	15.2	3.46	0.94
0.10	3.905(3)	3.763	17	20.0	3.20	1.00

Epitaxial qualities of the films were further characterized by high-angle annular dark field STEM (HAADF-STEM). The HAADF-STEM images of samples 004 and 010 are shown in Fig. 3.3(a) and (b). Well ordered interfaces between the film and the substrate are clearly visible. Fig. 3.3(c) shows the STEM electron energy loss spectroscopy (STEM-EELS) analysis of samples 004 and 010. This concentration profile is obtained by integration of the EELS intensity of the La- $M_{4,5}$ and Ti- $L_{2,3}$ edges during a spectrum image unit cell by unit cell in the growth direction. The profile is normalized by the maximum of intensity and cation vacancies are neglected. Identical intermixing (4 unit cells) was observed for both samples. This demonstrates that interdiffusion is a phenomenon that is not influenced by the growth pressure of the film.

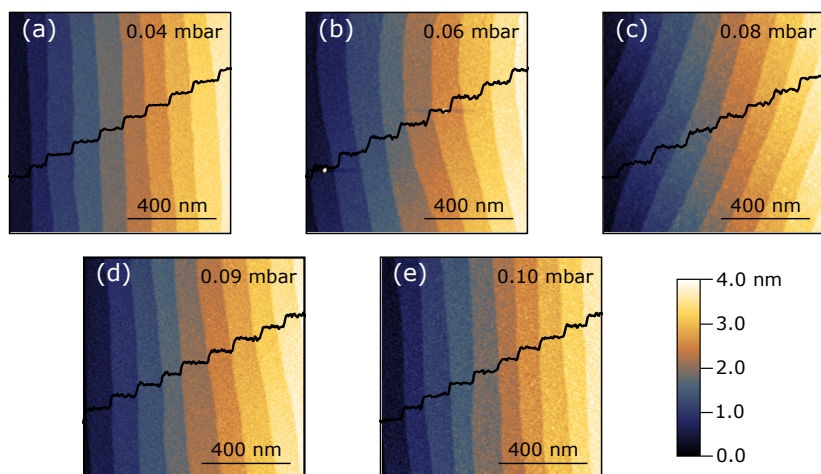


Figure 3.2: AFM topographic images of samples (a) 004, (b) 006, (c) 008, (d) 009 and (e) 010, using color code for the height. Insets are the height profiles of the surfaces.

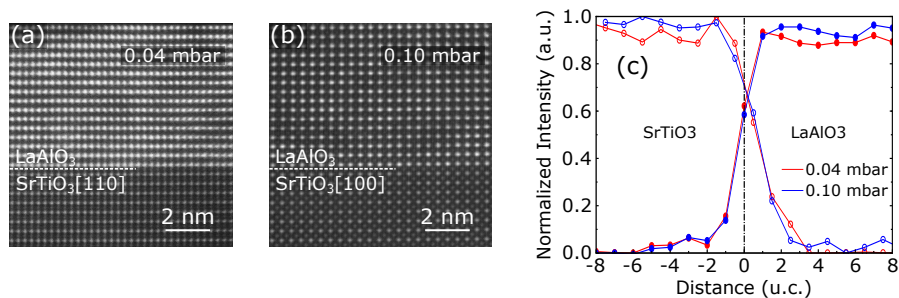


Figure 3.3: High-angle annular dark field STEM (HAADF-STEM) images of (a) sample 004 taken along the [110] direction and (b) sample 010 taken along the [100] direction. (c) STEM electron energy loss spectroscopy (STEM-EELS) analysis of samples 004 and 010, the $\text{La-M}_{4,5}$ (solid circles) and $\text{Ti-L}_{2,3}$ (open circles) edges integrated unit cell by unit cell across the interface. The data were acquired by D. Krishnan and N. Gauquelin at the University of Antwerp.

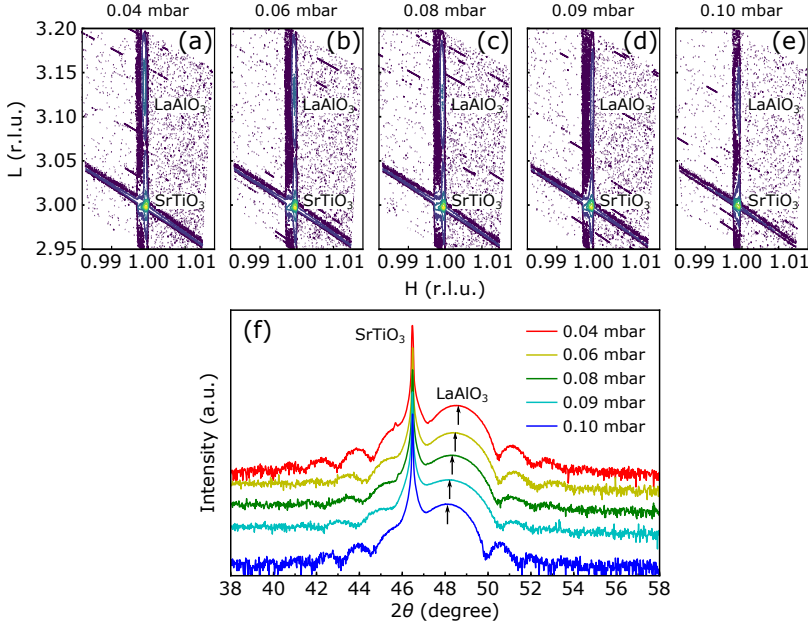


Figure 3.4: Reciprocal space maps (RSM) around the SrTiO_3 (103) diffraction peak of samples (a) 004, (b) 006, (c) 008, (d) 009 and (e) 010. (f) The θ - 2θ scans for samples grown at various Ar pressures. The black arrows are the LaAlO_3 (002) diffraction peaks.

3.3.2. X-ray diffraction

Fig. 3.4(a)-(e) show the reciprocal space maps (RSM) around the SrTiO_3 (103) diffraction peak of the five samples. The films are coherently strained to the substrates, which means that the in-plane lattice constants (a_{LAO}) are $\sim 3.905 \text{ \AA}$. Fig. 3.4(f) shows the θ - 2θ scans. The black arrows are the positions of the LaAlO_3 (002) diffraction peaks. It can be seen that as the sputtering pressure increases, the LaAlO_3 peak shifts to lower angle, which corresponds to an increase of the out-of-plane lattice constant (c_{LAO}) [119]. We extract c_{LAO} as well as the film thickness (t_{LAO}) by fitting the θ - 2θ scans. Table 3.1 summarizes the estimated values for a_{LAO} , c_{LAO} , t_{LAO} and the deposition rate of the five samples. It has been reported that the increase of c_{LAO} is due to the increase of the La/Al ratio in LaAlO_3 films. The relationship between them was systematically studied by Qiao *et al.* [119]. Thus, we obtain the La/Al ratios of our samples by interpolating our data points using their published results. The interpolated La/Al ratios are listed in Table 3.1. As the sputtering pressure increases from 0.04 to 0.10 mbar, the La/Al ratio increases from 0.88 to 1.00.

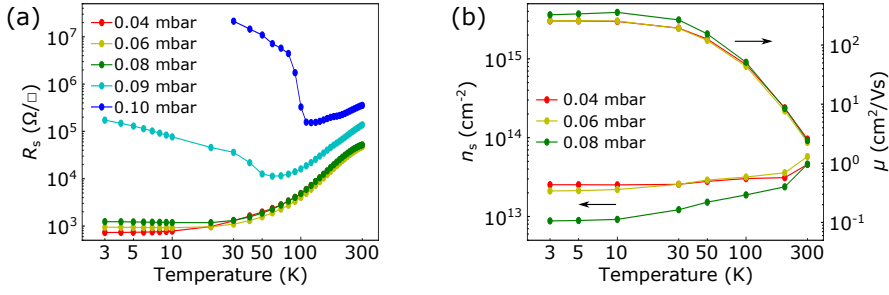


Figure 3.5: Temperature dependence of (a) the sheet resistance (R_s) and (b) the carrier density (n_s) and mobility (μ) for samples grown at various Ar pressures.

3.3.3. Transport properties

Fig. 3.5(a) shows the sheet resistance (R_s) as a function of temperature for samples grown at various Ar pressures. Samples 004, 006 and 008 show similar metallic behavior from 300 K to 3 K. The interfacial conductivity changes dramatically as the sputtering pressure further increases. For sample 009, R_s decreases from $1.4 \times 10^5 \Omega/\square$ at 300 K to $1.1 \times 10^4 \Omega/\square$ at 60 K and then gradually increases to $2.2 \times 10^5 \Omega/\square$ at 3 K. For sample 010, R_s decreases from $3.5 \times 10^5 \Omega/\square$ at 300 K to $1.6 \times 10^5 \Omega/\square$ at 100 K and abruptly changes to insulating state afterwards. The temperature dependence of the carrier density (n_s) and mobility (μ) for the metallic samples are shown in Fig. 3.5(b), which are determined by

$$n_s = \frac{B}{eR_{\text{Hall}}} \quad \text{and} \quad \mu = \frac{R_{\text{Hall}}}{BR_s(B=0)}. \quad (3.1)$$

The values of n_s and μ are approximately $1 \times 10^{13} \text{ cm}^{-2}$ and $2.6 \times 10^2 \text{ cm}^2/\text{Vs}$ at 3 K, respectively, which are consistent with reported results of the $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces grown by sputtering [103] and PLD [41, 46].

3.4. Discussion

Our observations are consistent with the results reported by Warusawithana *et al.* [59], namely only Al-rich LaAlO_3 gives rise to a conductive interface. All of our LaAlO_3 films are epitaxially strained to the SrTiO_3 substrates. Increasing the sputtering pressure only increases the La/Al ratio, which we believe is due to light Al being scattered more easily at higher pressures [54, 57]. The dramatic change in the transport properties is related to the change of cation stoichiometry of the LaAlO_3 films. For the $\text{LaAlO}_3/\text{SrTiO}_3$ samples grown by PLD, it has also been reported that a slight variation in growth parameters modifies the cation stoichiometry of LaAlO_3 [54–56], resulting in a dramatic change in the interfacial conductivity. But the cation stoichiometry is not checked on a routine

basis. It may explain the fact that samples from different PLD groups are often hardly comparable, although similar growth parameters are used.

Our results help to gain some insights into the origin of the 2DES. First, it is well known that La-doped SrTiO_3 shows metallic behavior [120]. At the $\text{LaAlO}_3/\text{SrTiO}_3$ interface, La/Sr intermixing could be induced in two ways. One way is simply by the PLD process itself, during which the SrTiO_3 substrate is bombarded by particles with kinetic energies around several tens of eV [32]. In our off-axis sputtering deposition, we use relatively high Ar pressures (0.04-0.10 mbar), which correspond to mean free paths of several millimeters. The direct distance between the center of the target and the substrate is about 87.5 mm. The ejected particles would undergo multiple scatterings to slow down their speed before they deposit on the substrate. In our case, the chance of introducing La/Sr intermixing by high energy particle bombarding should be low. The other way is the dipole compensation mechanism proposed by Nakagawa *et al.* [23], where a compensating dipole is produced by La/Sr intermixing to reduce the interface dipole energy. We observed identical intermixing in samples 004 and 010. However, the intermixing does not appear to be crucial to the origin of conductivity. Otherwise the two samples would show similar conductive behavior.

Next, we discuss other possible mechanisms for the interfacial conductivity. Based on DFT calculations, Warusawithana *et al.* [59] concluded that the driver of conductivity is electronic reconstruction. However, it cannot be reconciled with the experimental observation that stoichiometric LaAlO_3 films grown by MBE and sputtering give rise to insulating interfaces. The fact that conductivity is only observed in Al-rich films may point to the oxygen vacancies being the doping mechanism. In this scenario, the excess Al in Al-rich films getter oxygen from SrTiO_3 , which becomes *n*-type doped. Here we note that our samples grown in a mixture of Ar and O_2 show an insulating behavior. We suggest that the oxygen leads to oxidation of Al during the propagation towards the substrate [121], so that the Al is passivated and oxygen vacancies are not formed. The limited conductivity in stoichiometric LaAlO_3 films grown by PLD [54] can similarly be explained by defect generation induced by energetic particles in the ablation plume. On the other hand, we also observed that a conducting amorphous $\text{LaAlO}_3/\text{SrTiO}_3$ sample became insulating after post annealing in oxygen. This would indicate that the annealing treatment is efficient enough to remove the oxygen vacancies which are formed by the redox reaction [36]. It is therefore still not fully clear whether the observed conductivity in Al-rich samples is completely dominated by the oxygen vacancies formed in SrTiO_3 , but our observations on sputtered interfaces give good reasons to believe that the formation of oxygen vacancies is an important part of the puzzle.

3.5. Conclusion

In summary, high quality epitaxial LaAlO_3 films were grown on SrTiO_3 (001) substrates by 90° off-axis sputtering. While increasing the growth pressure, little structural variations have been observed, except for an increase of the out-of-plane lattice constant, which indicates an increase of the La/Al ratio. Metallic conductive interfaces were only found in Al-rich samples. Our results emphasize that cation stoichiometry in LaAlO_3 films plays an important role in the formation of interfacial conductivity at the $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces.

4

Electron trapping mechanism in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures

In $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures, a commonly observed but poorly understood phenomenon is that of electron trapping in back-gating experiments. In this Chapter, by combining magnetotransport measurements and self-consistent Schrödinger-Poisson calculations, we obtain an empirical relation between the amount of trapped electrons and the gate voltage. We find that the trapped electrons follow an exponentially decaying spatial distribution away from the interface. However, contrary to earlier observations, we find that the Fermi level remains well within the quantum well. The enhanced trapping of electrons induced by the gate voltage can therefore not be explained by a thermal escape mechanism. Further gate sweeping experiments strengthen our conclusion that the thermal escape mechanism is not valid. We propose a new mechanism which involves the electromigration and clustering of oxygen vacancies in SrTiO_3 . Our work indicates that electron trapping is a universal phenomenon in SrTiO_3 -based two-dimensional electron systems.

An adapted version of this Chapter has been submitted for publication in a peer-reviewed journal as C. Yin, A. E. M. Smink, I. Leermakers, L. M. K. Tang, N. Lebedev, U. Zeitler, W. G. van der Wiel, H. Hilgenkamp, and J. Aarts, *New insights into the electron trapping mechanism in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures*, arXiv preprint [122].

4.1. Introduction

The capability of controlling the electronic properties of a material by applying an external voltage is at the heart of modern electronics. In particular in oxide heterostructures, there is a constant search to manipulate their novel functionalities with an externally applied electric field [2]. The most well-known example is the high-mobility two-dimensional electron system (2DES) discovered at the interface between LaAlO_3 and SrTiO_3 [9]. The 2DES exhibits intriguing physical properties, such as superconductivity [6], signatures of magnetism [10, 11, 15] and even their coexistence [7, 12]. Additionally, due to the large permittivity of the SrTiO_3 substrate [123], the carrier density and mobility of the 2DES can be modulated by a back-gate voltage (V_G). Gate-tunable insulator to metal transitions [26], insulator to superconductor transitions [71] and Rashba spin-orbit interactions [18, 72] have been reported. At the $\text{LaAlO}_3/\text{SrTiO}_3$ interface, the 2DES is confined in a quantum well (QW) on the SrTiO_3 side and the band structure is formed by the Ti t_{2g} orbitals. For LaAlO_3 films grown on SrTiO_3 (001) substrates, the d_{xy} band lies below the $d_{xz,yz}$ bands in energy [61, 89, 124]. Applying V_G across the SrTiO_3 substrate changes the carrier density in the QW. A Lifshitz transition occurs when the Fermi level is tuned across the bottom of the $d_{xz,yz}$ bands [63], as discussed in Chapter 1 (see Fig. 1.5).

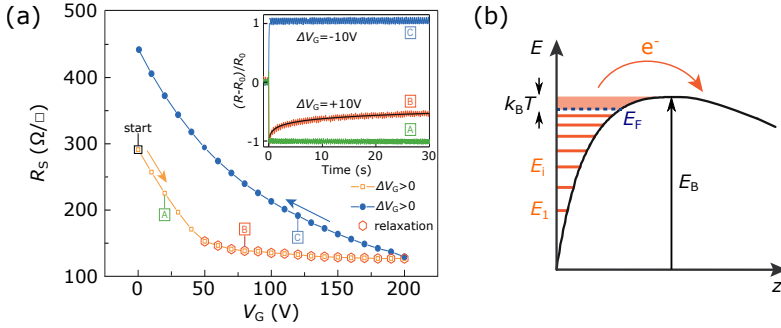


Figure 4.1: (a) Sheet resistance (R_s) as a function of gate voltage (V_G) at 4.2 K, as reported by Biscaras *et al.* [125]. Inset shows normalized resistance over time after a $\Delta V_G = \pm 10$ V step for points labeled "A", "B" and "C" in the main panel. (b) Schematic of the thermal escape mechanism where electrons escape from the quantum well beyond a filling threshold. Images adapted from Ref. [125].

In back-gating experiments, a commonly observed phenomenon is that the sheet resistance follows an irreversible route when V_G is swept first forward (increasing V_G) and then backward (decreasing V_G) [29, 71, 75, 86, 125–127], as shown in Fig. 4.1(a). The explanation as given by Biscaras *et al.* [125] is that the Fermi level lies intrinsically close to the top of the QW. High-mobility electrons escape from the QW and get trapped in SrTiO_3 when the carrier density is beyond a threshold, as depicted in Fig. 4.1(b). But the

relations between the amount of trapped electrons, their spatial distribution, and the back-gate voltage are still unknown.

In this Chapter, we study these relations by combining magnetotransport measurements and self-consistent Schrödinger-Poisson calculations. We find that the thermal escape mechanism cannot be reconciled with our results. We perform further gate sweep experiments which strengthen this conclusion. We propose a new mechanism which involves the electromigration and clustering of oxygen vacancies in SrTiO_3 .

4.2. Experiments

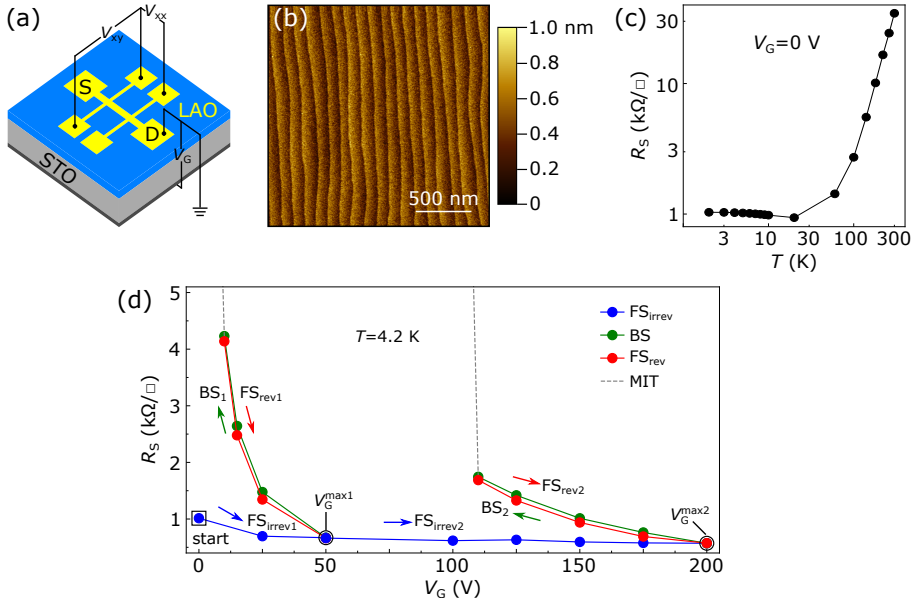


Figure 4.2: (a) Schematic of the Hall bar device. Source and drain are labeled as "S" and "D". The longitudinal voltage (V_{xx}) and transverse voltage (V_{xy}) are measured simultaneously. The gate voltage (V_G) is applied between the back of the substrate and the drain. (b) An AFM image of the LaAlO_3 surface taken at the Hall bar channel. (c) Temperature dependence of sheet resistance (R_S) with V_G grounded. (d) R_S as a function of V_G at 4.2 K. The solid circles are $R_S(B = 0)$. The blue, green and red arrows indicate the irreversible forward sweep (FS_{irrev}), backward sweep (BS), and reversible forward sweep (FS_{rev}), respectively. Two BSs were performed at 50 V ($V_G^{\text{max}1}$) and 200 V ($V_G^{\text{max}2}$). The gray dashed line indicates the metal-insulator transition (MIT).

The back-gating experiments were performed on a Hall bar device as depicted in Fig. 4.2(a). The Hall bar pattern was fabricated by photolithography as discussed in Chapter 2. The length between two voltage probes is $1000\text{ }\mu\text{m}$, and the Hall bar width is $150\text{ }\mu\text{m}$. 15 unit cells of LaAlO_3 film were deposited at 800°C and an Ar pressure of 0.04 mbar by 90° off-axis sputtering. Fig. 4.2 (b) shows an AFM image of the LaAlO_3 surface. The back-

gate electrode was formed by uniformly applying a thin layer of silver paint (Ted Pella, Inc.) on the back of the substrate. Magnetotransport measurements were performed under different V_G at 4.2 K in the Nijmegen cryostat. The longitudinal voltage (V_{xx}) and transverse voltage (V_{xy}) were measured simultaneously by standard lock-in technique ($f = 13.53$ Hz and $i_{\text{RMS}} = 1.0 \mu\text{A}$). The maximum applied V_G was +200 V and the leakage current was less than 1 nA during the measurement.

The device was cooled down to 4.2 K with V_G grounded as plotted in Fig. 4.2(c). The sheet resistance R_s as a function of V_G is shown in Fig. 4.2(d). V_G was first increased from 0 V to 50 V (V_G^{max1}), resulting in a decrease of R_s . This sweep is called an irreversible forward sweep (FS_{irrev}), because R_s increased above the virgin curve when V_G was swept backward. The backward sweep (BS) led to a metal-insulator transition (MIT)¹, which is consistent with earlier reports [86]. After the onset of the MIT, defined from the phase shift of the lock-in amplifier increasing above 15°, V_G was further decreased to completely deplete the QW. When V_G was swept forward again, R_s followed the same route as the BS. Therefore the latter forward sweep is named a reversible forward sweep (FS_{rev}). Another BS was performed at 200 V (V_G^{max2}). It can be seen that R_s increased faster in BS₁ than in BS₂. The reason of which will be discussed later.

4

4.3. Back-gate tuning of magnetotransport properties

Fig. 4.3(a)-(h) demonstrate the back-gate tuning of magnetotransport properties in various regimes. Besides a weak antilocalization signature in low magnetic fields² [72] (Fig. 4.3(a)-(d)), we observed the characteristic features of the Lifshitz transition [63], namely a positive magnetoresistance, $\text{MR} = [R_s(B)/R_s(0) - 1] \times 100\%$, in high magnetic fields (Fig. 4.3(a)-(d)) and a nonlinear Hall resistance (Fig. 4.3(e)-(h)). To extract the carrier density and mobility as a function of V_G , we fitted the magnetotransport data with a two-band model [128]

$$R_s = \frac{1}{e} \cdot \frac{\frac{n_1 \mu_1}{1 + (\mu_1 B)^2} + \frac{n_2 \mu_2}{1 + (\mu_2 B)^2}}{\left(\frac{n_1 \mu_1}{1 + (\mu_1 B)^2} + \frac{n_2 \mu_2}{1 + (\mu_2 B)^2} \right)^2 + \left(\frac{n_1 \mu_1^2 B}{1 + (\mu_1 B)^2} + \frac{n_2 \mu_2^2 B}{1 + (\mu_2 B)^2} \right)^2}, \quad (4.1)$$

$$R_{xy} = \frac{B}{e} \frac{\frac{n_1 \mu_1^2}{1 + \mu_1^2 B^2} + \frac{n_2 \mu_2^2}{1 + \mu_2^2 B^2}}{\left(\frac{n_1 \mu_1}{1 + \mu_1^2 B^2} + \frac{n_2 \mu_2}{1 + \mu_2^2 B^2} \right)^2 + \left(\frac{n_1 \mu_1^2 B}{1 + \mu_1^2 B^2} + \frac{n_2 \mu_2^2 B}{1 + \mu_2^2 B^2} \right)^2}, \quad (4.2)$$

where n_1 and n_2 are the carrier densities of the first and second conduction bands, respectively, and μ_1 and μ_2 are the corresponding mobilities. We note that n_1 has the d_{xy}

¹We note that the MIT can be observed in Hall bar devices, but not in unpattered samples measured by the van der Pauw method. See Fig. 4.9 in the supplemental material for more details.

²The weak antilocalization effect will be discussed in more detail in Chapter 5.

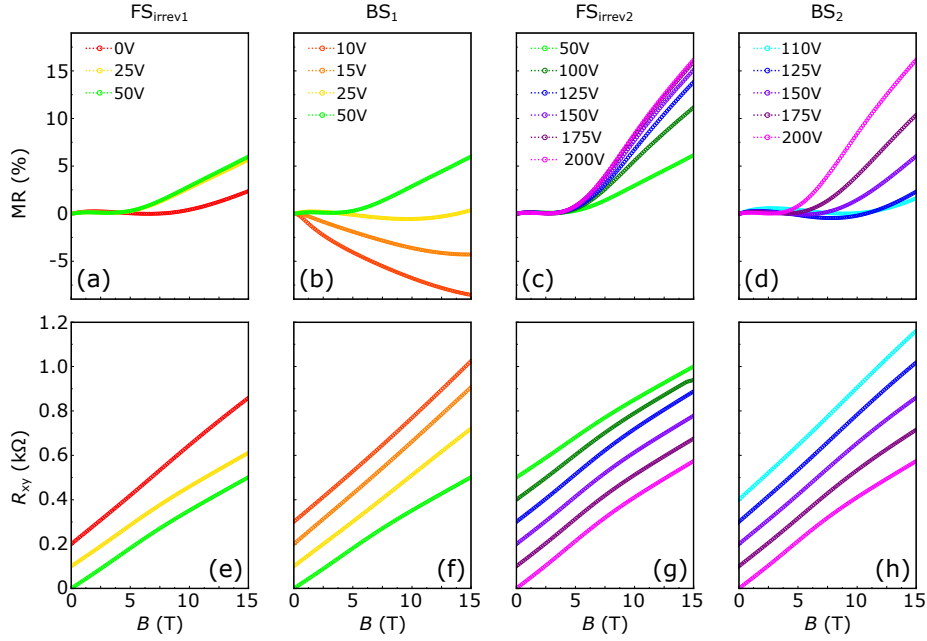


Figure 4.3: (a)-(d) Magnetoresistance, $MR = [R_s(B)/R_s(0) - 1] \times 100\%$, as a function of magnetic field, B , in various regimes: (a) FS_{irrev1}, (b) BS₁, (c) FS_{irrev2} and (d) BS₂. (e)-(h) Hall resistance, R_{xy} , as a function of B in various regimes: (e) FS_{irrev1}, (f) BS₁, (g) FS_{irrev2} and (h) BS₂. Curves are separated by an offset of 100 Ω for clarity. The results of FS_{rev} regimes are similar to that of BS regimes, which are therefore omitted.

character and n_2 has the $d_{xz,yz}$ character. The total carrier density, n_{tot} , is the sum of n_1 and n_2 .

It can be seen in Fig. 4.4(a) and (b) that only the d_{xy} band was occupied at 0 V. In FS_{irrev1}, electrons were added into the QW and the Lifshitz transition occurred at a carrier density (n_L) of $1.51 \times 10^{13} \text{ cm}^{-2}$, which is close to earlier reported values [63]. In BS₁, n_{tot} decreased to $1.33 \times 10^{13} \text{ cm}^{-2}$ at 10 V, which is the onset of the MIT, comparable to the earlier reported carrier density ($0.5\text{--}1.5 \times 10^{13} \text{ cm}^{-2}$) for the MIT [129]. In FS_{rev1}, the carrier densities of the bands were tuned reversibly as in BS₁ and the system was fully recovered when 50 V was reapplied. In FS_{irrev2}, n_{tot} almost saturated at $2.17 \times 10^{13} \text{ cm}^{-2}$ beyond 125 V. In BS₂, the MIT occurred at 110 V with a carrier density of $1.65 \times 10^{13} \text{ cm}^{-2}$, which could be due to the Hall bar contacts becoming insulating faster than the channel [90]. A noteworthy feature is that the amount of gate-induced trapped electrons is independent of the number of backward sweeps and is only related to $V_G^{\max}$.

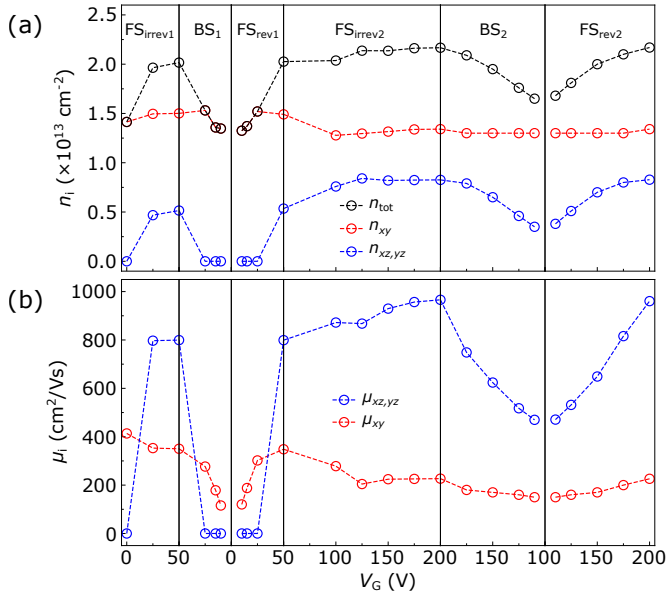


Figure 4.4: (a) Carrier density as a function of V_G in various regimes. The red and blue circles represent the carrier density of the d_{xy} band (n_{xy}) and the $d_{xz,yz}$ band ($n_{xz,yz}$). The black circle is the total carrier density (n_{tot}), which is the sum of n_{xy} and $n_{xz,yz}$. (b) Corresponding values for the mobility in various regimes.

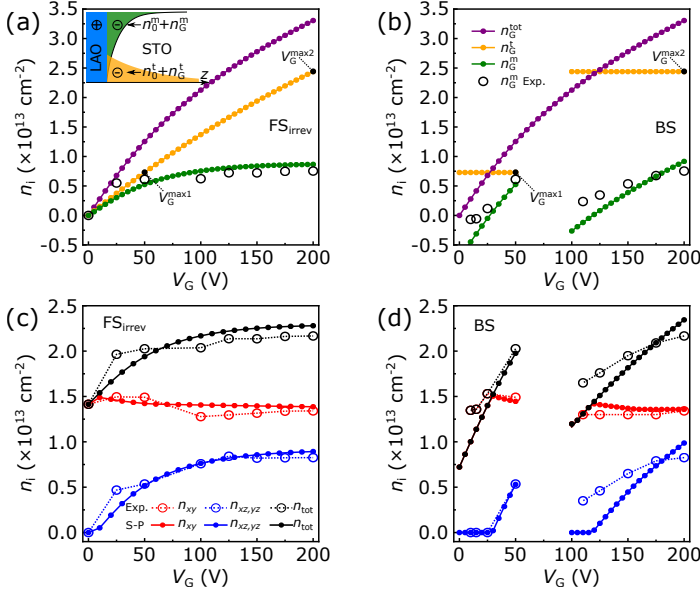


Figure 4.5: (a)-(b) V_G dependence of the calculated gate-induced total charge density (n_G^{tot} , purple), trapped charge density (n_G^{tr} , yellow), mobile charge density (n_G^{m} , green) and measured gate-induced mobile charge density (n_G^{m} Exp., open black circle) in (a) FS_{irrev} and (b) BS regimes. The inset of (a) shows an illustration of the interface for Schrödinger-Poisson (S-P) calculations. (c)-(d) V_G dependence of S-P calculated (solid circles) and measured (open circles) n_{xy} (red), $n_{xz,yz}$ (blue) and n_{tot} (black) in (a) FS_{irrev} and (b) BS regimes.

4.4. Schrödinger-Poisson calculations

First, we study the relation between the amount of trapped electrons and the gate voltage. In a back-gating experiment, the total amount of electrons (n_G^{tot}) induced by V_G , as shown by the purple curves in Fig. 4.5(a) and (b), can be calculated using a parallel plate capacitor model [130, 131]:

$$n_G^{\text{tot}}(V_G) = \int_{V_1}^{V_2} \frac{\epsilon_0}{ed_{\text{STO}}} \epsilon_r(V_G) dV_G, \quad (4.3)$$

where ϵ_0 is the vacuum permittivity, e is the electron charge and d_{STO} is the thickness of the SrTiO₃ substrate (0.5 mm). The field-dependent permittivity of the SrTiO₃ substrate $\epsilon_r(V_G)$ is calculated following Ref. [132]:

$$\epsilon_r(E) = 1 + \frac{B}{[1 + (E/E_0)^2]^{1/3}}, \quad (4.4)$$

where the electric field $E = V_G/d_{\text{STO}}$, $B = 25462$ and $E_0 = 82213$ V/m. In FS_{irrev} regimes, as shown in Fig. 4.5(a), a part of n_G^{tot} becomes gate-induced trapped electrons (n_G^{tr}) in SrTiO₃. Subtracting n_G^{tr} from n_G^{tot} will give the amount of gate-induced mobile electrons

(n_G^m) which are doped into the QW. We find that the relation between n_G^{tr} and V_G can be described using the following expression:

$$n_G^{\text{tr}}(V_G) = N(1 - e^{-\frac{V_G}{400}}), \quad (4.5)$$

which yields the yellow curve, where $N = 6.2 \times 10^{13} \text{ cm}^{-2}$. The subtraction ($n_G^{\text{tot}} - n_G^{\text{tr}} = n_G^m$) is given by the green curve, and gives a good description of the measured n_G^m (open black circle). In BS regimes, as shown in Fig. 4.5(b), n_G^{tot} is given by V_G according to Eq. (4.3). However, the value of n_G^{tr} is fixed at the $n_G^{\text{tr}}(V_G^{\text{max}})$. Thus, n_G^m is smaller than its counterpart in FS_{irrev} regimes. In both BS regimes the calculated n_G^m is in good agreement with the experimental data. Moreover, due to the field-dependent permittivity, dn_G^{tot}/dV_G is decreasing as V_G increases. As a consequence, the same negative ΔV_G removes more mobile electrons at 50 V than at 200 V, which could explain the fact that R_s increases faster in BS_1 than in BS_2 . It should be noted that the empirical formula of $n_G^{\text{tr}}(V_G)$ is not universal, but instead varies among samples. We performed similar V_G sweeps on two reference samples and observed slightly different V_G dependence of R_s (See Fig. 4.10 in the supplemental material for more details.). Thus, $n_G^{\text{tr}}(V_G)$ should always be obtained from experimental results.

Next, we study the spatial distribution of the trapped electrons. The self-consistent Schrödinger-Poisson (S-P) model is a tool to study the charge distribution and band occupation [89, 128, 133–135]. S-P calculations are based on the effective mass and envelope wave function approximations³. Due to the orbital orientation, d_{xy} and $d_{xz,yz}$ orbitals are heavy and light in the z direction, respectively. Here, we take the effective mass as $m_{xy}^{*z} = 14 m_e$ and $m_{xz,yz}^{*z} = 0.7 m_e$ [89, 124, 134], where m_e is the electron rest mass. We take $z > 0$ to be SrTiO_3 and $z < 0$ to be LaAlO_3 , as shown in the inset of Fig. 4.5(a). In the original state, there are initial mobile electrons (n_0^m , $1.41 \times 10^{13} \text{ cm}^{-2}$ in our sample) and initial trapped electrons (n_0^{tr}) on the SrTiO_3 side, and an equivalent amount of positive charges on the LaAlO_3 side to keep overall charge neutrality.

The spatial distributions of the trapped electrons, both n_0^{tr} and $n_G^{\text{tr}}(V_G)$, are input parameters of the S-P model, which effectively influence the V_G dependent occupation of the d_{xy} and $d_{xz,yz}$ bands. In our calculations, we obtain the best results by using the following distribution of the trapped electrons:

$$n_{3D}^{\text{tr}}(z, V_G) = \begin{cases} 0 & \text{for } z < 0 \\ \frac{n_0^{\text{tr}} + n_G^{\text{tr}}(V_G)}{\lambda} e^{-\frac{z}{\lambda}} & \text{for } z \geq 0 \end{cases} \quad (4.6)$$

where $n_0^{\text{tr}} = 6.4 \times 10^{13} \text{ cm}^{-2}$ and $\lambda = 50 \text{ nm}$. The integration range is from 0 nm to 100 nm, which is divided into 2000 equal sections. The calculated evolutions of n_{xy} and $n_{xz,yz}$ in

³A detailed description of the self-consistent Schrödinger-Poisson calculation can be found in Appendix A.

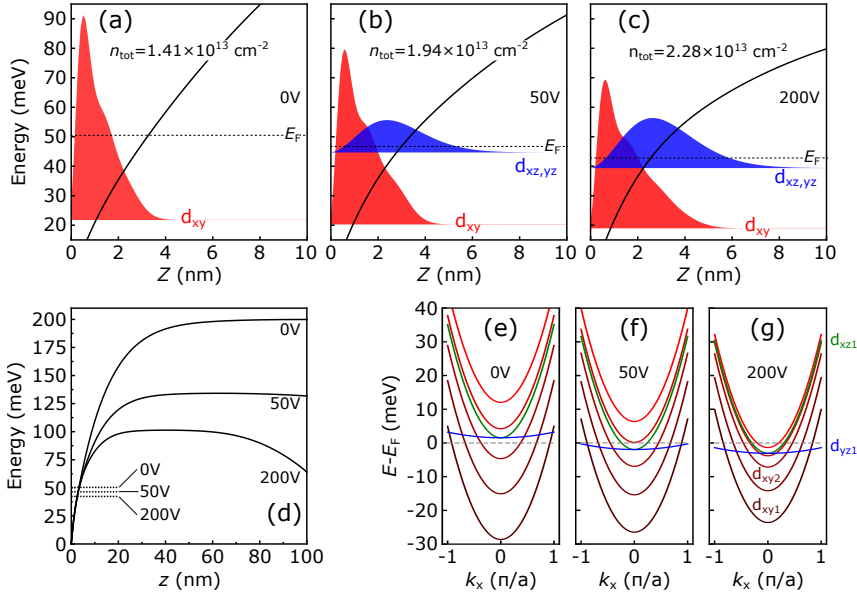


Figure 4.6: (a)-(c) S-P calculated confining potential profile (solid line), Fermi energy (dotted line), and spatial distribution of mobile electrons occupying d_{xy} (red) and $d_{xz,yz}$ (blue) bands at (a) 0V, (b) 50V and (c) 200V. (d) S-P calculated confining potential profile and Fermi energy in a larger range. (e)-(f) S-P calculated subband dispersions in parabolic approximation at (e) 0V, (f) 50V and (g) 200V.

FS_{irrev} and BS regimes are shown in Fig. 4.5(c) and (d), closely agreeing with the experimental data.

Based on the above analysis, we could obtain the confining potential profile, the Fermi energy and the spatial distribution of mobile electrons occupying the d_{xy} and $d_{xz,yz}$ bands. Fig. 4.6(a)-(c) show the results at 0V, 50V and 200V, respectively. The mobile electrons are confined within ~ 10 nm at the interface, which agrees with the reported spatial distribution of the 2DES [44, 136, 137]. Fig. 4.6(d) shows the confining potential in a larger range. It can be seen that in all cases the Fermi level is well below the top of the QW, therefore the probability of mobile electrons thermally escaping ($k_B T (4.2 \text{ K}) \approx 0.36 \text{ meV}$) from the QW should be very low. The subband dispersions of the three cases are shown in Fig. 4.6(e)-(g). We note that increasing V_G decreases the spacing between the subband levels.

4.5. Revaluation of thermal escape mechanism

In order to check the thermal escape mechanism [125] in more detail, we warmed up the device to room temperature to remove the electron trapping effect [29]. The device

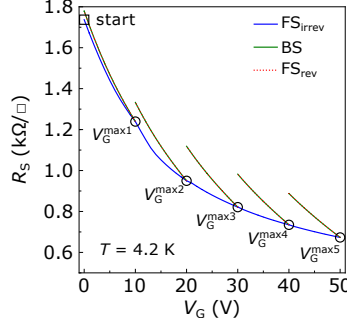


Figure 4.7: V_G dependence of R_s at 4.2 K. Backward sweeps were performed from 10 V to 50 V. Note that BS and FS_{rev} overlap perfectly.

4

was cooled down to 4.2 K again and multiple backward sweeps were performed from 10 V to 50 V. As shown in Fig. 4.7, a growing R_s separation between FS_{irrev} and BS can be clearly seen as V_G^{max} increases. In the thermal escape mechanism, it is stated that electron trapping only occurs after R_s (or n_{tot}) reaches its saturation. However, our experiment clearly shows that electron trapping occurs immediately when positive V_G is applied and the amount of trapped electrons increases as V_G^{max} increases. So we can rule out the thermal escaping of mobile electrons to be the mechanism for electron trapping. Moreover, similar irreversible behavior has been also reported in other 2DES, such as $\text{LaTiO}_3/\text{SrTiO}_3$ [125], $\text{LaVO}_3/\text{SrTiO}_3$ [75], $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.7}/\text{SrTiO}_3$ [138] and amorphous $\text{LaAlO}_3/\text{SrTiO}_3$ [139]. Therefore the electron trapping phenomenon must be intrinsic to the SrTiO_3 substrate.

4.6. Discussion

We propose a two-step trapping mechanism which involves the redistribution of oxygen vacancies (V_{O}) in SrTiO_3 under influence of an electric field. The first step is the electromigration of V_{O} . Among all types of defects in SrTiO_3 , V_{O} has the lowest activation enthalpy for migration [140]. Electromigration of V_{O} in SrTiO_3 has also been reported in previous works [141–143]. The second step is the clustering of V_{O} . It has been calculated that V_{O} clustering could form in-gap trapping states [144, 145], of which the energy was recently determined to be ~ 0.31 eV and ~ 1.11 eV below the conduction band [146]. Fig. 4.8 shows the dynamic resistance change during and after V_G sweeps in the FS_{irrev} and BS regimes. The electron trapping mechanism can then be explained as follows. In FS_{irrev} regimes as shown in Fig. 4.8(a), the effect of increasing V_G is twofold. One is to add electrons into the QW. The other is to push positively charged V_{O} s migrating toward the interface. The clustering of the accumulated V_{O} s then forms in-gap trapping

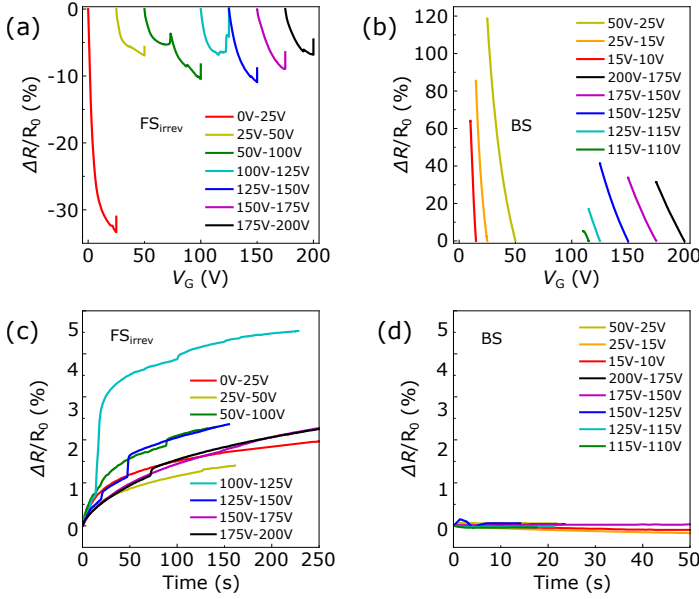


Figure 4.8: (a)-(b) Dynamic change of R_s during V_G sweeps in (a) FS_{irrev} and (b) BS regimes. V_G was swept at a rate of 0.1 V/s. R_s measurements kept on going for several minutes after the stabilization of V_G . (c)-(d) Dynamic change of R_s after V_G sweeps in (c) FS_{irrev} and (d) BS regimes.

states. Several sudden resistance jumps can be clearly seen during V_G sweeps, which might be due to the formation of big V_O clusters. Moreover, after stabilizing the gate voltage as shown in Fig. 4.8(c), the electromigration and clustering of V_O s do not stop immediately. Newly formed in-gap states still trap conduction electrons, resulting in an immediate increase of R_s when V_G stabilizes. In BS and FS_{rev} regimes as shown in Fig. 4.8(b) and (d), sweeping V_G only changes the carrier density in the QW without modifying the defect landscape near the interface. Therefore the system can be tuned in a reversible manner.

4.7. Conclusion

In summary, we have studied the electron trapping phenomenon in LaAlO₃/SrTiO₃ heterostructures under back-gate voltages. By combining magnetotransport measurements and self-consistent Schrödinger-Poisson calculations, we have identified a relation between the amount of trapped electrons and the gate voltage as well as the spatial distribution of the trapped electrons. We have proposed a new trapping mechanism which involves the electromigration and clustering of oxygen vacancies in SrTiO₃, since our analysis shows that the thermal escape mechanism is not valid. Our work improves

the understanding of back-gating experiments in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures. It is also valuable for theoretical works [134, 147, 148], where the assumption was that all the gate-induced electrons land in the QW. This assumption clearly needs to be reconsidered. Equally importantly, our work indicates that electron trapping is a universal phenomenon in SrTiO_3 -based two-dimensional electron systems, which is instructive to future applications of complex oxide electronic devices.

Supplemental material

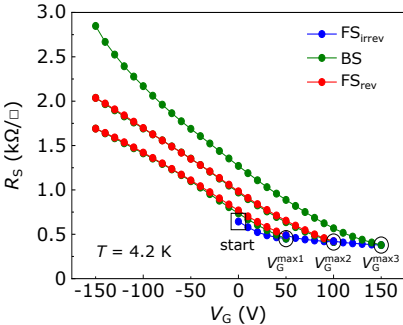


Figure 4.9: Sheet resistance (R_s) as a function of gate voltage (V_G) at 4.2 K measured on an unpatterned sample by the van der Pauw method. Backward sweeps performed at 50 V, 100 V and 150 V, respectively.

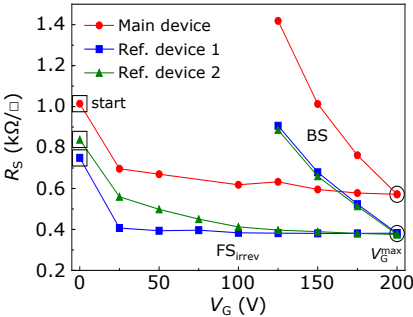


Figure 4.10: Sheet resistance (R_s) as a function of gate voltage (V_G) at 4.2 K measured on two reference devices. Backward sweep performed at 200 V.

5

Tuning Rashba spin-orbit coupling in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures by band filling

The electric-field tunable Rashba spin-orbit coupling at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface shows potential applications in spintronic devices. However, different gate dependence of the coupling strength has been reported in experiments. On the theoretical side, it has been predicted that the largest Rashba effect appears at the crossing point of the d_{xy} and $d_{xz,yz}$ bands. In this Chapter, we study the tunability of the Rashba effect in $\text{LaAlO}_3/\text{SrTiO}_3$ by means of back-gating. The Lifshitz transition was crossed multiple times by tuning the gate voltage so that the Fermi energy is tuned to approach or depart from the band crossing. By analyzing the weak antilocalization behavior in the magnetoresistance, we find that the maximum spin-orbit coupling effect occurs when the Fermi energy is near the Lifshitz point. Moreover, we find strong evidence for a single spin winding at the Fermi surface.

An adapted version of this Chapter has been submitted for publication in a peer-reviewed journal as C. Yin, P. Seiler, L. M. K. Tang, I. Leermakers, N. Lebedev, U. Zeitler, and J. Aarts, *Tuning Rashba spin-orbit coupling at $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces by band filling*, arXiv preprint [149].

5.1. Introduction

Complex oxide heterostructures provide an interesting platform for novel physics since their physical properties are determined by the correlated d electrons [2]. The most famous example is the discovery of a high-mobility two-dimensional electron system (2DES) at the interface between LaAlO_3 and SrTiO_3 [9]. Intriguing properties, such as superconductivity [6], signatures of magnetism [10, 11, 15] and even their coexistence [7, 12], have been reported.

At the $\text{LaAlO}_3/\text{SrTiO}_3$ interface, the 2DES is confined in an asymmetric quantum well (QW) in SrTiO_3 . The intrinsic structure inversion asymmetry introduces an electric field which gives rise to a Rashba spin-orbit (SO) coupling [150]. Additionally, due to the large permittivity of the SrTiO_3 substrate at cryogenic temperatures [123], the coupling constant can be tuned with the SrTiO_3 as back gate [18, 72, 74, 75]. This could give rise to applications in spintronics, such as spin field-effect transistors [151]. However, the reported results are inconsistent. Upon increasing the back-gate voltage (V_G), the SO coupling strength was found to decrease [18], increase [72, 74], or show a maximum [75]. A clear understanding of the SO coupling dependence on V_G is necessary for more advanced experiments.

For a free electron gas the Rashba spin splitting is proportional to the symmetry breaking electric field, however the Rashba effect in solids like semiconductor and oxide heterostructures has a more complicated origin [152]. Theoretical studies have shown that multiorbital effects play an essential role in the SO coupling in $\text{LaAlO}_3/\text{SrTiO}_3$ [64, 153, 154]. At the $\text{LaAlO}_3/\text{SrTiO}_3$ (001) interface, the band structure is formed by the Ti t_{2g} orbitals. At the Γ -point, the d_{xy} band lies below the $d_{xz,yz}$ bands in energy [124]. Applying V_G across the SrTiO_3 substrate changes the carrier density and therefore the Fermi energy (E_F). A Lifshitz transition occurs when E_F is tuned across the bottom of the $d_{xz,yz}$ bands [63]. The largest SO coupling effect was predicted at the crossing point of the d_{xy} and $d_{xz,yz}$ orbitals [64, 153, 154]. The SO coupling theory was experimentally confirmed later by angle-resolved photoemission spectroscopy (ARPES) measurements [155].

So far, few experiments actually track the evolution of SO coupling when E_F is driven to approach or depart from the Lifshitz point. In this Chapter, we study the Rashba effect in back-gated $\text{LaAlO}_3/\text{SrTiO}_3$. By carefully monitoring the sign of the magnetoresistance in high magnetic field and the linearity of the Hall resistance, V_G was tuned back and forth so that the Lifshitz transition was crossed multiple times. The SO coupling characteristic magnetic fields were extracted by fitting the weak antilocalization (WAL) behavior in the magnetoresistance (MR). We find that the maximum SO coupling effect occurs when E_F is near the Lifshitz point. We also find a single spin winding at the Fermi surface.

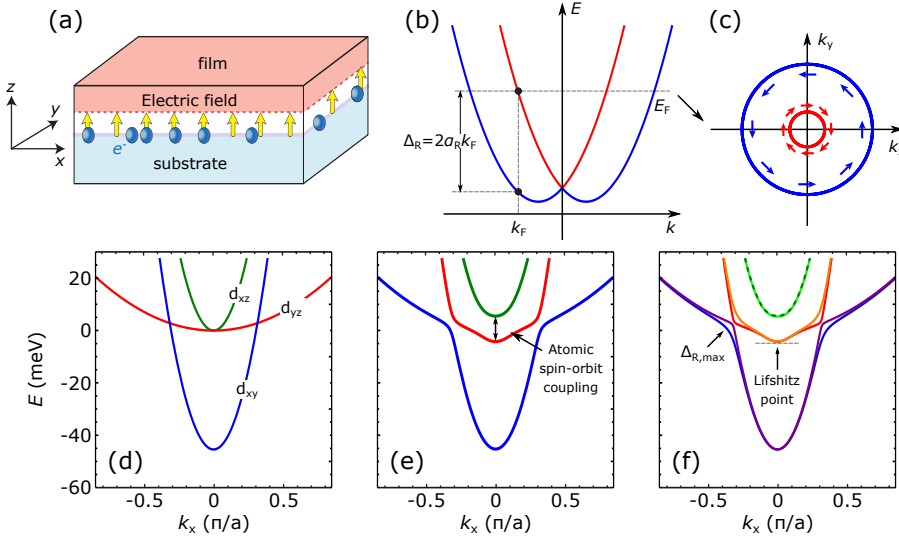


Figure 5.1: (a) Structural inversion symmetry breaking in heterostructures. The built-in electric field along the growth direction breaks the inversion symmetry, resulting in the SO coupling. (b) Band dispersion of a nearly free two-dimensional electron gas due to Rashba SO coupling. (c) The corresponding Fermi surface. The spins are locked to their momenta and counter-propagating electrons have opposite spins. Images adapted from Ref. [157]. (d)-(f) Effective three-band model at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface. (d) Spin-degenerate t_{2g} bands. (e) The t_{2g} bands with atomic SO coupling included. The three bands are still double degenerate. (f) The t_{2g} bands with atomic SO coupling and inversion asymmetry included. Maximum spin splitting is at the crossing point of the d_{xy} and $d_{xz,yz}$ orbitals. The Lifshitz point is at the bottom of the $d_{xz,yz}$ bands. Images adapted from Ref. [64].

5.2. Theoretical concepts

5.2.1. Rashba spin-orbit coupling in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures

SO coupling is most familiar in atomic physics, which describes the coupling between an electron's spin and its orbital angular momentum about the nucleus [156]. It enters into the Hamiltonian as a relativistic correction to the Schrödinger equation, giving rise to the SO term [152]

$$H_{SO} = -\frac{\hbar}{4m_e^2 c^2} \vec{\sigma} \cdot \vec{p} \times \vec{\nabla} V, \quad (5.1)$$

where $\hbar$ is the Planck constant, m_e is the mass of a free electron, c is the speed of light, $\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ is the vector of Pauli spin matrices, $\vec{p}$ is the kinetic momentum and V is the electric potential of the atomic core. It can be understood from Eq. (5.1) that the electric field produced by the charged nucleus gives rise to a magnetic field in the reference frame moving with an orbiting electron, resulting in a momentum-dependent effective Zeeman energy.

In condensed matter systems, electrons move in a crystal potential. SO coupling arises when there is a potential gradient on average. There are usually two types of SO couplings in condensed matter systems. The first one is the Dresselhaus SO coupling which originates from the bulk inversion asymmetry (BIA), as for instance in zinc blende structures [158]. The second one is the Rashba SO coupling which is due to the structure inversion asymmetry (SIA) in heterostructures [150]. Here we focus on the Rashba SO coupling. First, let's consider a heterostructure with a nearly free two-dimensional electron gas, as depicted in Fig. 5.1(a). The built-in electric field, $\vec{E} = E_z \vec{z}$, breaks the symmetry between the z and $-z$ direction, resulting in a Rashba SO coupling of the form [159]

$$H_R = \frac{\alpha_R}{\hbar} \vec{\sigma} \cdot \vec{p} \times \vec{z}, \quad (5.2)$$

where α_R is known as the Rashba parameter and $\vec{z}$ is the unit vector in the z direction. As shown in Fig. 5.1(b) the spin-degenerate states are split and the eigenvalues are

$$\epsilon_{\pm}(k) = \frac{\hbar^2 k^2}{2m^*} \pm \alpha_R k, \quad (5.3)$$

where k is the wavevector and m^* is the effective mass. The spin texture at the Fermi surface is plotted in Fig. 5.1(c). The spin polarization is always perpendicular to $\vec{k}$ and counter-propagating electrons have opposite spins. The Rashba spin splitting Δ_R is given by

$$\Delta_R = 2\alpha_R k_F \quad (5.4)$$

where k_F is the Fermi wavevector. Since α_R is proportional to the interfacial electric field, it seems that Δ_R can be linearly tuned by an externally applied electric field. According to Eq. (5.4), however, a typical electric field in experiments, e.g. 100 V, only yields $\Delta_R \sim 10^{-8}$ meV [153], which is much smaller than the measured values at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface that are of the order of meV [18, 72].

By considering the interplay between atomic SO coupling and inversion asymmetry, theoretical studies have predicted that the maximum Rashba effect is at the crossing point of the d_{xy} and $d_{xz,yz}$ orbitals [64, 153, 154], as shown in Fig. 5.1(d)-(f). In magnetotransport measurements, it is hard to estimate where the band crossing is. However, the Lifshitz point locating at the bottom of the $d_{xz,yz}$ bands is very close to the band crossing as shown in Fig. 5.1(f). Therefore, by carefully monitoring the characteristic features of the Lifshitz transition, one can nicely tune the relative position between the Fermi energy and the band crossing.

5.2.2. Weak localization and weak antilocalization effects

SO coupling can be experimentally studied from the weak antilocalization (WAL) effect in magnetotransport measurements. To understand WAL, we first introduce the weak

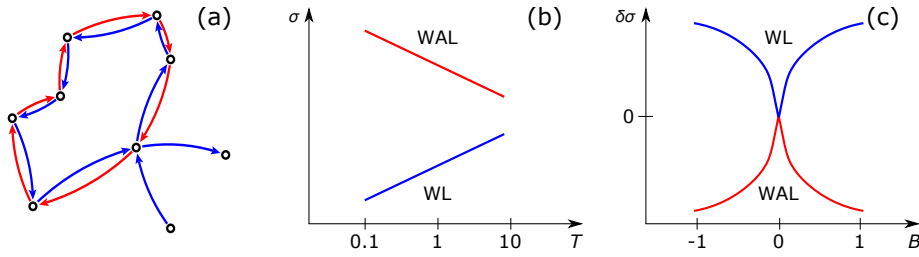


Figure 5.2: (a) Schematic of the time-reversed closed-loop trajectory pairs of electrons. The quantum interference between them becomes important when the phase coherence length is much greater than the mean free path, $l_\phi \gg l$. (b)-(c) Signatures of weak localization (WL) and weak antilocalization (WAL). (b) Temperature dependence of the conductivity σ . (c) Magnetoconductivity, $\delta\sigma = \sigma(B) - \sigma(0)$. Images adapted from Ref. [161].

localization (WL) effect. In a weakly disordered system, the electrons motion is diffusive rather than ballistic. The electronic transport is related to two characteristic lengths [160]: (i) The mean free path l , which measures the average distance that an electron travels before its momentum is changed by elastic scattering from static scattering centers. (ii) The phase coherence length l_ϕ , which measures the average distance an electron can maintain its phase coherence. l_ϕ is determined by inelastic scattering from electron-phonon and electron-electron interactions. If $l \geq l_\phi$, the system is in the classical diffusive regime and the conductivity is described by the Drude model. If $l \ll l_\phi$, the system is in the quantum diffusive regime since electrons maintain their phase coherence even after being scattered for many times. In this regime, the constructive quantum interference between time-reversed pairs of electrons with closed-loop trajectories, as shown in Fig. 5.2(a), will reduce the Drude conductivity. The effect of this quantum correction is called WL. In the presence of SO coupling, the electron spin is locked to its momentum. The two time-reversed paths gain an extra phase of π . The destructive quantum interfere between the two paths will then enhance the Drude conductivity. This opposite effect of WL is called WAL.

The conductivity correction from quantum interference is related to l and l_ϕ by a logarithmic function

$$\sigma^{\text{qi}} \propto \pm \frac{e^2}{\pi h} \ln \frac{l_\phi}{l}, \quad (5.5)$$

where e^2/h is the conductance quantum, "-" corresponds to WL and "+" to WAL. In Eq. (5.5), l is determined by the elastic scattering which is temperature independent, while l_ϕ is determined by the inelastic scattering which is usually a function of temperature, and empirically, $l_\phi \propto T^{-p/2}$, where p is positive and depends on scattering mechanism and dimensionality [162]. When lowering temperature, σ^{qi} will become prominent, which gives the temperature dependence of the conductivity as shown in

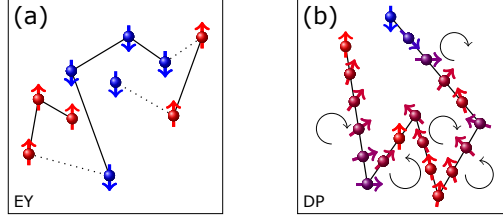


Figure 5.3: (a) Schematic of the Elliott-Yafet (EY) mechanism. Scatterings from impurities or phonons rarely flip the electron's spin. (b) Schematic of the D'yakonov-Perel' (DP) mechanism. Electron's spin continuously precesses around the internal magnetic field due to SO coupling. Arrows indicate directions of the Larmor precession. Image adapted from Ref. [170].

Fig. 5.2(b). When applying a magnetic field, the time-reversal symmetry will be broken. Since σ^{qi} is due to the quantum interference between the two time-reversed loops, it will be destroyed in a magnetic field, giving rise to the magnetoconductivity as shown in Fig. 5.2(c), which is the characteristic feature of WL and WAL.

Next, we discuss two theories for analyzing WAL, namely the HLN theory, developed by Hikami, Larkin and Nagaoka [163], and the ILP theory, developed by Iordanskii, Lyanda-Geller and Pikus [164]. The qualitative results of both theories are similar, however, the physical picture behind them are very different.

The HLN model considers the Elliott-Yafet (EY) spin relaxation mechanism [165, 166], which operates in systems with an inversion symmetry, such as silicon [167]. In the EY mechanism, the spin relaxation is due to momentum scattering from impurities or phonons. In the presence of SO coupling, the Bloch states are a mixture of spin-up and spin-down states. The degree of admixture depends on the electron's wavevector, making the electron's spin orientation dependent on its momentum. Any momentum scattering gives a probability of flipping the spin, leading to spin relaxation. The spin relaxes during the scattering as shown in Fig. 5.3(a), therefore the faster is the momentum scattering, the faster is the spin relaxation [168].

The ILP model considers the D'yakonov-Perel' (DP) spin relaxation mechanism [169], which operates in systems with a broken inversion symmetry. In the DP mechanism, SO coupling manifests itself as a momentum-dependent magnetic field. An electron moving with one velocity feels one effective magnetic field along which the electron's spin precesses. When a scattering event occurs, the electron changes its velocity and it feels a different (in both magnitude and direction) SO magnetic field. The spin performs a kind of random walk, with the spin flip occurring if the spin manages to walk as far as the opposite from its original orientation. Unlike the EY mechanism, the spin relaxes in between the scattering events as shown in Fig. 5.3(b), therefore the more scattering events there are, the less is the spin relaxation [168].

5.3. Experiments

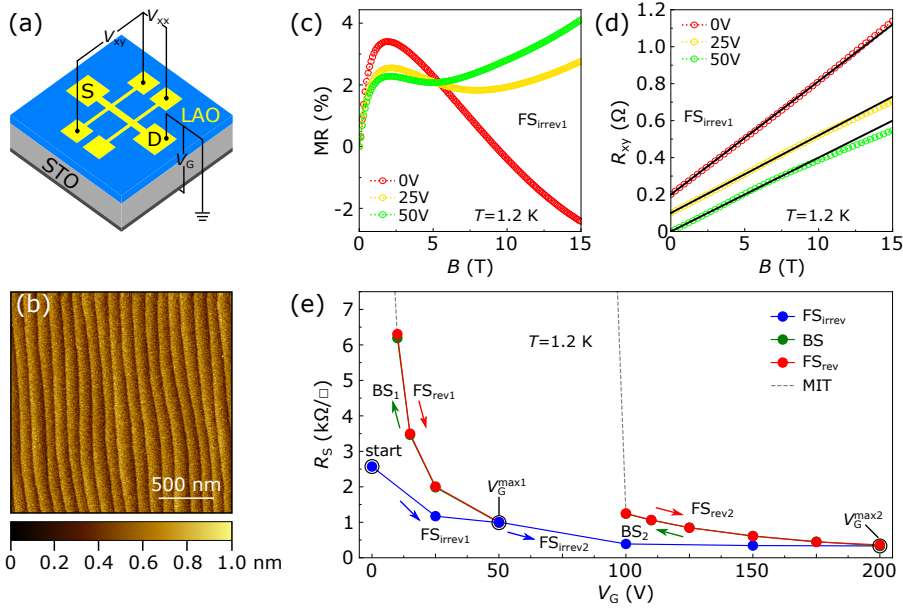


Figure 5.4: (a) Schematic of the Hall bar device. Source and drain are labeled as "S" and "D". The longitudinal voltage (V_{xx}) and transverse voltage (V_{xy}) are measured simultaneously. The gate voltage (V_G) is applied between the back of the substrate and the drain. (b) An AFM image of the LaAlO_3 surface taken at the Hall bar channel. (c) Magnetoresistance, $\text{MR} = [R_s(B)/R_s(0) - 1] \times 100\%$, as a function of magnetic field, B , in the first irreversible forward sweep ($\text{FS}_{\text{irrev1}}$) regime at 1.2 K. (d) Hall resistance, R_{xy} , as a function of B in $\text{FS}_{\text{irrev1}}$ at 1.2 K. Curves are separated by an offset of $100\ \Omega$ for clarity. Black lines are linear fits to $R_{xy}(B)$. (e) Sheet resistance (R_s) as a function of V_G at 1.2 K. The solid circles are $R_s(B = 0)$. The blue, green and red arrows indicate the irreversible forward sweep (FS_{irrev}), backward sweep (BS), and reversible forward sweep (FS_{rev}), respectively. Two BSs were performed at 50 V (V_G^{max1}) and 200 V (V_G^{max2}). The gray dashed line indicates the metal-insulator transition (MIT).

The back-gating experiments were performed on a Hall bar device as depicted in Fig. 5.4(a). The Hall bar pattern was fabricated by photolithography as discussed in Chapter 2. The length between two voltage probes is $1000\ \mu\text{m}$, and the Hall bar width is $150\ \mu\text{m}$. 15 unit cells of LaAlO_3 film were deposited at $800\ ^\circ\text{C}$ and an Ar pressure of $0.04\ \text{mbar}$ by 90° off-axis sputtering. Fig. 5.4 (b) shows an AFM image of the LaAlO_3 surface. The back-gate electrode was formed by uniformly applying a thin layer of silver paint (Ted Pella, Inc.) on the back of the substrate. Magnetotransport measurements were performed under different V_G at 1.2 K in the Nijmegen cryostat. The longitudinal voltage (V_{xx}) and transverse voltage (V_{xy}) were measured simultaneously by standard lock-in technique ($f = 13.53\ \text{Hz}$ and $i_{\text{RMS}} = 1.0\ \mu\text{A}$). The maximum applied V_G was $+200\ \text{V}$ and the leakage

current was less than 1 nA during the measurement.

The device was first cooled down to 1.2 K with V_G grounded. In the original state ($V_G = 0$ V), the observed maximum in MR (Fig 5.4(c)) in low magnetic fields shows the signature of WAL [72]. The negative MR in high magnetic fields as well as the approximately linear Hall resistance (R_{xy}) (Fig 5.4(d)) indicate that the presence of only one type of carriers. Next, V_G was increased to add electrons to the QW and two characteristic Lifshitz transition features appeared at 25 V. They are the emergence of positive MR in high magnetic field and the change of linearity of $R_{xy}(B)$ [63, 89]. V_G was further increased to 50 V (V_G^{max1}) to drive E_F slightly above the Lifshitz point, resulting in larger positive MR and more downward bending of R_{xy} in high magnetic fields.

Then V_G was decreased to remove electrons from the QW in order to go back through the Lifshitz transition from the high-density direction. In Chapter 4, we have shown that due to the effect of electron trapping in SrTiO_3 , the sheet resistance (R_s) always follows an irreversible route when V_G is first swept forward and then backward. Fig. 5.4(e) shows R_s as a function of V_G . It can be seen that R_s increases above the virgin curve when V_G is swept backward. The backward sweep finally leads to a metal-insulator transition (MIT), whose onset is defined from the phase shift of the lock-in amplifier increasing above 15° . Sweeping V_G forward again results in a reversible decrease of R_s which overlaps with the previous backward sweep and the system is fully recovered when V_G is reapplied to 50 V. We therefore classify V_G sweeps into three regimes, namely irreversible forward sweep (FS_{irrev}), backward sweep (BS) and reversible forward sweep (FS_{rev}). V_G was then increased to 200 V (V_G^{max2}) to drive E_F well above the Lifshitz point. Similar reversible behavior is observed in BS₂ and FS_{rev2}.

5

5.4. Back-gate tuning of magnetotransport properties

Fig. 5.5(a)-(h) demonstrate the back-gate tuning of magnetotransport properties in various regimes. Besides the signature of WAL and characteristic features of the Lifshitz transition, we also observed small upturns in R_{xy} in intermediate magnetic fields. The Hall coefficient, $R_H = R_{xy}/B$ in various regimes is plotted in Fig. 5.5(i)-(l). A similar feature has also been reported by other groups [63, 171], but its origin is still under debate. There are attempts to relate it to an unconventional anomalous Hall effect (AHE) [172] or hole transport [171], however we cannot get convincing fits using these models. To extract the carrier density and mobility as a function of V_G , we fitted the magnetotransport data with a two-band model [128]

$$R_s = \frac{1}{e} \cdot \frac{\frac{n_1 \mu_1}{1 + (\mu_1 B)^2} + \frac{n_2 \mu_2}{1 + (\mu_2 B)^2}}{\left(\frac{n_1 \mu_1}{1 + (\mu_1 B)^2} + \frac{n_2 \mu_2}{1 + (\mu_2 B)^2} \right)^2 + \left(\frac{n_1 \mu_1^2 B}{1 + (\mu_1 B)^2} + \frac{n_2 \mu_2^2 B}{1 + (\mu_2 B)^2} \right)^2}, \quad (5.6)$$

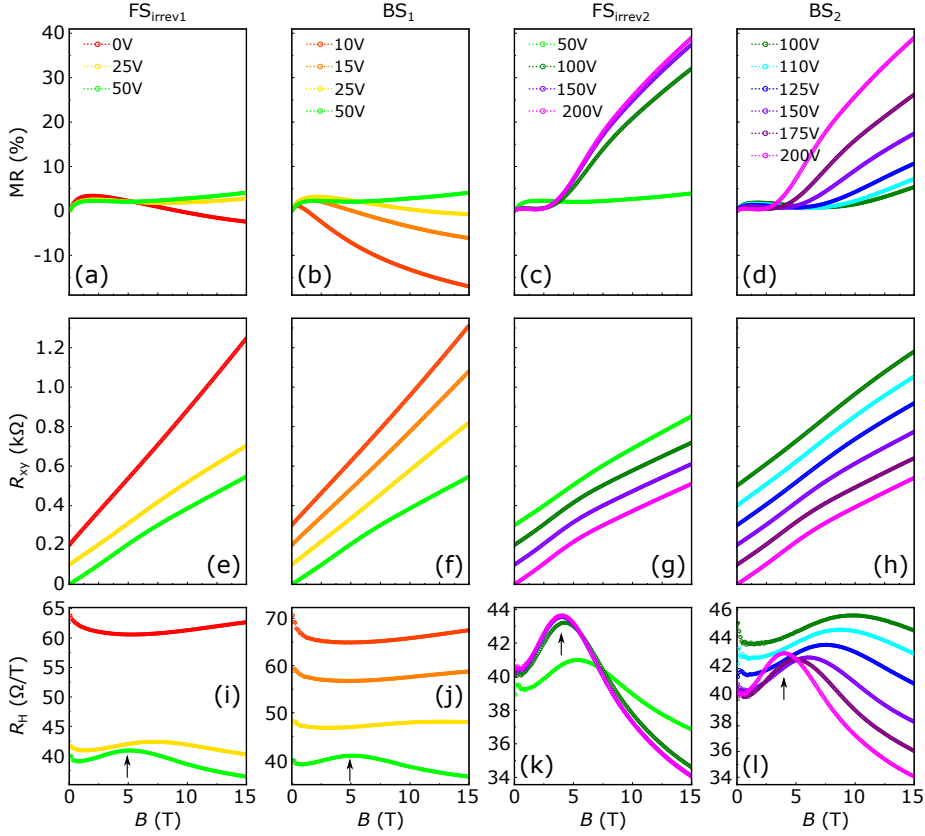


Figure 5.5: (a)-(d) Magnetoresistance, MR, as a function of magnetic field, B , in various regimes: (a) FS_{irrev1} , (b) BS_1 , (c) FS_{irrev2} and (d) BS_2 . (e)-(h) Hall resistance, R_{xy} , as a function of B in various regimes: (e) FS_{irrev1} , (f) BS_1 , (g) FS_{irrev2} and (h) BS_2 . Curves are separated by an offset of 100 Ω for clarity. (i)-(l) Hall coefficient, $R_H = R_{xy}/B$, as a function of B in various regimes: (i) FS_{irrev1} , (j) BS_1 , (k) FS_{irrev2} and (l) BS_2 . Black arrows indicate the small upturns in R_{xy} . The results of FS_{rev} regimes are similar to that of BS regimes, which are therefore omitted.

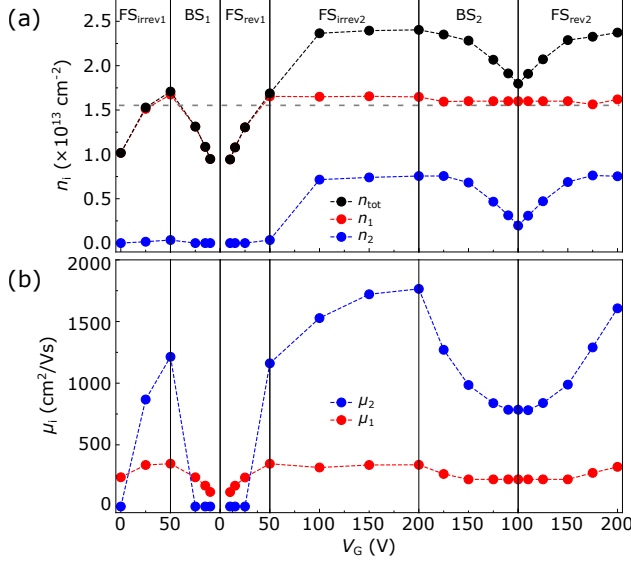


Figure 5.6: (a) V_G dependence of carrier densities. n_1 and n_2 stand for that of the low mobility carriers (LMC) and high mobility carriers (HMC), respectively. The total carrier density (n_{tot}) is the sum of n_1 and n_2 . The gray dash line represent the critical carrier density ($n_L = 1.51 \times 10^{13} \text{ cm}^{-2}$) for Lifshitz transition. (b) V_G dependence of mobilities, that of the LMC and HMC are labeled as μ_1 and μ_2 , respectively.

$$R_{xy} = \frac{B}{e} \frac{\frac{n_1 \mu_1^2}{1 + \mu_1^2 B^2} + \frac{n_2 \mu_2^2}{1 + \mu_2^2 B^2}}{\left(\frac{n_1 \mu_1}{1 + \mu_1^2 B^2} + \frac{n_2 \mu_2}{1 + \mu_2^2 B^2}\right)^2 + \left(\frac{n_1 \mu_1^2 B}{1 + \mu_1^2 B^2} + \frac{n_2 \mu_2^2 B}{1 + \mu_2^2 B^2}\right)^2}, \quad (5.7)$$

where n_1 and n_2 are the carrier densities of the first and second conduction bands, respectively, and μ_1 and μ_2 are the corresponding mobilities. For a reliable convergence n_2 and μ_2 are set to 0 in the one-band transport regime. We note that n_1 has the d_{xy} character and n_2 has the $d_{xz,yz}$ character. The total carrier density, n_{tot} , is the sum of n_1 and n_2 . The small upturns in R_{xy} cannot be captured by the two-band model, however, we emphasize that the extraction of the transport parameters is not affected strongly by this feature.

As shown in Fig. 5.6(a), the critical carrier density (n_L) corresponding to the Lifshitz transition is $1.51 \times 10^{13} \text{ cm}^{-2}$, which is close to earlier reported results [63]. The evolution of the carrier densities indicates that E_F approaches the Lifshitz point in regimes FS_{irrev1}, FS_{rev1} and BS₂ and departs from the Lifshitz point in regimes BS₁, FS_{irrev2} and FS_{rev2}. In Fig. 5.6(b), it can be seen that μ_1 almost stays unaffected above the Lifshitz transition whereas μ_2 can be considerably changed tuned by V_G , reaching $\sim 1800 \text{ cm}^2/\text{Vs}$ at 200 V.

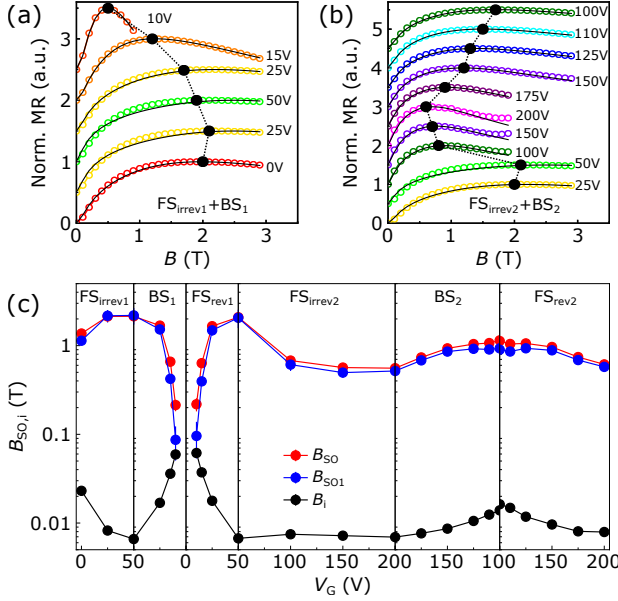


Figure 5.7: (a)-(b) Weak antilocalization (WAL) analysis of the magnetoresistance (MR) in regimes (a) FS_{irrev1} and BS_1 and (b) FS_{irrev2} and BS_2 . The solid circles correspond to experimental data and black lines to fits using the ILP model. The local maximum of each MR curve is plotted black. The MR curves are normalized to the local maxima and separated by an offset of 0.5. The black dashed line is a guide to the eye for the evolution of the local maxima. (c) Fitted characteristic magnetic fields as a function of V_G . SO field B_{SO} is the sum of B_{SO1} (single spin winding) and B_{SO3} (triple spin winding). B_i is the inelastic scattering field. WAL analyses were performed by P. Seiler.

5.5. Weak antilocalization analysis

In low-dimensional systems, the conductivity shows signatures of quantum interference between time-reversed closed-loop electron trajectory pairs. In the presence of SO coupling the pairs interfere destructively, leading to a positive MR in low magnetic field which is known as the WAL [173]. For a system with Rashba-type of SO coupling, the spin relaxation is described by the DP mechanism [169]. The model for analyzing the WAL was established by Iordanskii, Lyanda-Geller and Pikus (ILP) [164]. In this model, both the single and triple spin winding contributions at the Fermi surface have been taken into account. It should be noted that the ILP model is an effective single-band model, which means that above the Lifshitz point the fitted characteristic magnetic field for SO coupling is an effective field for both the d_{xy} and $d_{xz,yz}$ bands. A model that considers multi-band effects is not available yet. The WAL correction to the magnetoconductivity

is given by [164, 171, 174, 175]:

$$\Delta\sigma(B) = -\frac{e^2}{2\pi h} [\mathcal{L}(B) - \mathcal{L}(0) + \psi(\frac{1}{2} + \frac{B_i}{B}) - \ln(\frac{B_i}{B})], \quad (5.8)$$

where ψ is the digamma function, and

$$\begin{aligned} \mathcal{L}(B) = \frac{1}{a_0} + \frac{2a_0 + 1 + \frac{B_{\text{SO1}} + B_{\text{SO3}}}{B}}{a_1(a_0 + \frac{B_{\text{SO1}} + B_{\text{SO3}}}{B}) - 2\frac{B_{\text{SO1}}}{B}} \\ + \sum_{n=1}^{\infty} \frac{3a_n^2 + 2a_n \frac{B_{\text{SO1}} + B_{\text{SO3}}}{B} - 1 - 2(2n+1)\frac{B_{\text{SO1}}}{B}}{(a_n + \frac{B_{\text{SO1}} + B_{\text{SO3}}}{B})a_{n-1}a_{n+1} - 2\frac{B_{\text{SO1}}}{B}[(2n+1)a_n - 1]}, \end{aligned} \quad (5.9)$$

where

$$a_n = n + \frac{1}{2} + \frac{B_i + B_{\text{SO1}} + B_{\text{SO3}}}{B}. \quad (5.10)$$

The fitting parameters are the characteristic magnetic fields for the inelastic scattering $B_i = \hbar/4eD\tau_i$, and for the spin-orbit coupling $B_{\text{SO}n} = (\hbar/4eD)2\Omega_n^2\tau_n$ ($n = 1$ or 3 for single or triple spin winding), where D is the diffusion constant, τ_i and τ_n are relaxation times, and Ω_n is spin splitting coefficient.

Fig. 5.7(a) and 5.7(b) depict WAL fits of the MR in the two FS_{irrev} and BS regimes. The solid black circles represent the local maxima of the MR curves. In principle, the SO coupling strength can be roughly estimated by the magnetic field (B_{max}) where the local maximum appears [75]. It can be clearly seen that B_{max} increases as E_F approaches the Lifshitz point (regimes $\text{FS}_{\text{irrev1}}$ and BS_2), while B_{max} decreases as E_F departs from the Lifshitz point (regimes BS_1 and $\text{FS}_{\text{irrev2}}$). The fitted values for the characteristic magnetic fields are plotted in Fig. 5.7(c), where B_{SO} is the sum of B_{SO1} and B_{SO3} . In most cases B_{SO3} is much smaller than B_{SO1} , indicating a single spin winding at the Fermi surface. It can be seen that B_{SO1} rises almost an order of magnitude in FS_{rev1} , and then goes down by a factor of 2 in $\text{FS}_{\text{irrev2}}$. The maximum SO coupling strength occurs near the Lifshitz point, agreeing with the evolution of B_{max} . Driving E_F either above or below the Lifshitz point would lead to a decrease of the SO coupling strength. B_i increases when the carrier density is lowered, which is due to more accessible phonons contributing to the scattering process, and vice versa.

If B_{SO1} is 0 and only B_{SO3} is present, the ILP formula could be reduced to the simpler model developed by Hikami, Larkin and Nagaoka (HLN) [163], in which the spin relaxation is described by the EY mechanism [165, 166]. However, the HLN model yields inaccurate fits to our data, which is different from earlier reported results [75, 176], where a triple spin winding has been found. We also tried the model suggested by Maekawa and Fukuyama (MF) [177], which takes the Zeeman splitting into account. However, the MF model also gives inaccurate fits. Fig. 5.8(a)-(c) show the comparison between the fitting

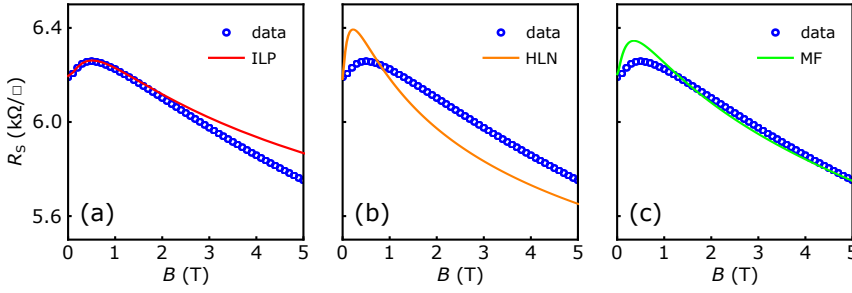


Figure 5.8: WAL analysis to the MR curve measured at 10 V in BS₁ from different models. (a) ILP model. (b) HLN model. (c) MF model. WAL analyses were performed by P. Seiler.

results from the three models. The WAL feature in low magnetic fields is nicely caught by the ILP model.

5.6. Conclusion

In summary, we have performed magnetotransport measurements to study the Rashba spin-orbit coupling effect in back-gated LaAlO₃/SrTiO₃. By tuning the gate voltage, the Fermi energy has been driven to approach or depart from the Lifshitz point multiple times. We have done weak antilocalization analysis of the magnetoresistance using the ILP model, which reveals a single spin winding at the Fermi surface. We have found that the maximum Rashba effect occurs when the Fermi energy is near the Lifshitz point, and that the change of the characteristic field on the low carrier density side is larger than the high carrier density side. Our experiments have manifested the nontrivial Rashba effect predicted by theoretical works. Applying an external electric field can tune the coupling strength, but its direct contribution is rather small. Instead the gating effect is indirect. It is the tuning of carrier densities and therefore band filling that significantly influence the Rashba effect. Driving the Fermi energy above or below the Lifshitz point would result in a decrease of the coupling strength. Our findings provide valuable insights to the investigation and design of oxide-based spintronic devices.

6

Tunable magnetic interactions in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures by ionic liquid gating

The gating effect achieved by an ionic liquid and its electric double layer allows for charge transfer which can be an order of magnitude larger than with conventional dielectrics. However, the large charged ions also causes inevitable Coulomb scattering in the conducting channel formed at the interface, which can limit the carrier mobility enhancement. In this Chapter, we study the effect of the LaAlO_3 thickness on the transport properties in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures by ionic liquid gating. We find that the transport properties of the $\text{LaAlO}_3/\text{SrTiO}_3$ interface are dominated by the intrinsic interactions rather than the LaAlO_3 thickness and possible effects from the ions in the liquid. We observe a Kondo effect, which is enhanced while increasing the gate voltage. We also observe a gate-tunable and temperature-dependent anomalous Hall effect, which always emerges near the Kondo temperature. Our experiments pave the way to manipulate the various magnetic interactions in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures.

An adapted version of this Chapter has been submitted for publication in a peer-reviewed journal as C. Yin, K. Prateek, W. Gelling, and J. Aarts, *Tunable magnetic interactions in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures by ionic liquid gating*, arXiv preprint [178].

6.1. Introduction

The two-dimensional electron system (2DES) at the interface between LaAlO_3 and SrTiO_3 [9] has been the focus of intensive studies due to its intriguing properties, such as superconductivity [6], signatures of magnetism [10, 11, 15] and even their coexistence [7, 12]. The 2DES properties can also be modulated by electrostatic gating. Pioneering works have been performed in the back-gate configuration, where the dielectric insulator is the SrTiO_3 substrate. Novel gate-tunable effects, such as insulator to metal transition [26], insulator to superconductor transition [71] and Rashba spin-orbit coupling [18, 72] have been reported. However, in this configuration high voltages of tens to hundreds of volts are required to achieve a sizable gating effect. Moreover, the high voltages also induce unavoidable modifications to the defect landscape in the SrTiO_3 substrate as discussed in Chapter 4. The top-gate geometry works in a similar way as the back-gate counterpart, but the insulating dielectric is the LaAlO_3 overlayer. Compared with back-gating, the big advantage of top-gating is that it requires very low voltages to achieve sizeable gating effects. However, the device fabrication process is very complicated which is due to the requirement of multiple aligned lithography steps [91].

6

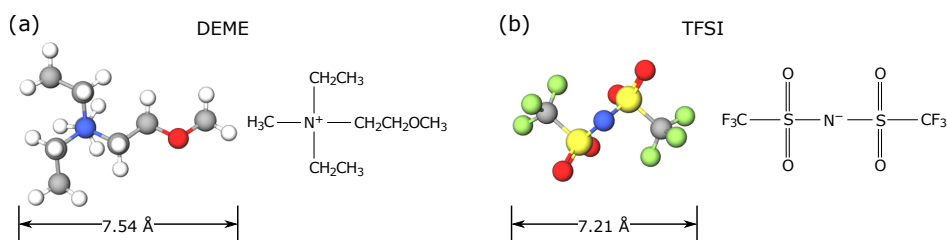


Figure 6.1: Molecular structures and molecular formulas of (a) positively charged DEME and (b) negatively charged TFSI. Average diameters of DEME and TFSI are 7.54 Å and 7.21 Å, respectively [179].

Electric double layer transistors (EDLTs) of the top-gate configuration provide an alternative approach. In recent years, EDLTs have generated considerable research interest due to the capability of inducing high carrier densities in materials. EDLTs have been used for inducing superconductivity in SrTiO_3 [94] and KTaO_3 [95] as well as for tuning transport properties in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures [70, 99, 100]. EDLTs use ionic liquids (ILs) as gate dielectrics, in which the size of the ions is usually larger than the lattice parameter of perovskite oxides. For instance, the average diameter of the ions in a widely used IL, called DEME-TFSI¹ as shown in Fig. 6.1, is about 7 Å [179]. When the electrolyte touches the channel, the long-range Coulomb potentials created by the ions

¹Molecular formula is N,N-diethyl-N-methyl-N-(2-methoxyethyl)-ammonium bis-trifluoromethylsulfonyl-imide

will cause inevitable scattering of the conduction electrons and therefore limit the mobility enhancement, as was shown for experiments on BN-encapsulated graphene [180]. In a similar fashion, Gallagher *et al.* [181] have recently reported a ten-fold improvement of the carrier mobility in SrTiO_3 single crystals by covering the channel with a thin BN flake.

In $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures, the LaAlO_3 film is a natural protection for the channel. However, one would expect that there is a trade-off between obtaining high carrier densities, which requires thin LaAlO_3 layers, and achieving high mobilities, which requires thick LaAlO_3 layers. In this Chapter, we study the effect of the LaAlO_3 film thickness on the transport properties of three $\text{LaAlO}_3/\text{SrTiO}_3$ EDLTs. We obtain the largest tunability in a device with about 4 unit cells (uc) of LaAlO_3 . We observe a gate-tunable Kondo effect in all the devices. More interestingly, we also observe a temperature-dependent nonlinearity of the Hall resistance, which is always accompanied by the emergence of a Kondo effect. We attribute this anomaly to an anomalous Hall effect. Our results imply that the transport properties of $\text{LaAlO}_3/\text{SrTiO}_3$ EDLTs are mainly governed by the intrinsic interactions, while the LaAlO_3 thickness has a minor effect.

6.2. Experiments

A schematic of the EDLT device is shown in Fig. 6.2(a). The Hall bar pattern was fabricated by photolithography as discussed in Chapter 2. The length between two voltage probes is $500\text{ }\mu\text{m}$, and the Hall bar width is $50\text{ }\mu\text{m}$. It is well known that the critical thickness of LaAlO_3 which gives rise to a conducting interface is 4 uc [26]. We fabricated three devices with difference thickness of LaAlO_3 layer by using the calibrated growth rate of $4.3\text{ }\text{\AA}/\text{min}$ to estimate the thickness. Growth times were 3.5, 7.0 and 10.5 min, respectively, yielding the devices with thicknesses of 1.5, 3.0 and 4.5 nm, which we refer to as 4uc, 8uc and 12uc. The LaAlO_3 films were deposited at 800°C and an Ar pressure of 0.04 mbar by 90° off-axis sputtering. Fig. 6.2(b)-(d) depict the AFM images of the LaAlO_3 surface of the three devices. After sample fabrication, a droplet of IL, DEME-TFSI (IO-LITEC) was applied onto the device surface covering the gate electrode and the channel.

The magnetotransport measurements were performed in the PPMS at temperatures down to 3 K. As shown in Fig. 6.2(a), a Keithley 6221 current source was used to apply a direct current ($I_{\text{DC}} = 1.0\text{ }\mu\text{A}$). Two Keithley 2182A nanovoltmeters were used to measure the longitudinal (V_{xx}) and transverse voltages (V_{xy}). The gate voltage (V_{G}) was applied by a Keithley 2400 source meter. The freezing point of DEME-TFSI is $\sim 180\text{ K}$. As a general procedure, we applied V_{G} at 210 K and then waited for $\sim 15\text{ min}$ for the IL to equilibrate. The measurements were started at 150 K and the leakage current was less than 1.0 nA during the measurements.

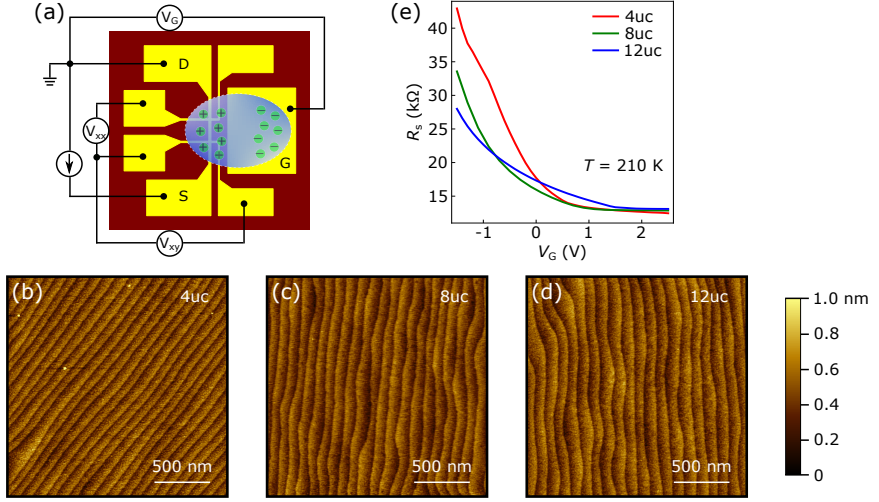


Figure 6.2: (a) Schematic of the EDLT device. Source and drain are labeled as "S" and "D". The longitudinal (V_{xx}) and transverse voltages (V_{xy}) are measured simultaneously. Gate voltage (V_G) is applied between the gate electrode ("G") and the drain. (b)-(d) AFM images of the LaAlO_3 surface taken at the Hall bar channel of devices (b) 4uc, (c) 8uc and (d) 12uc. (e) Sheet resistance (R_s) as a function of V_G at 210 K of the three devices with different thickness of the LaAlO_3 layer as indicated.

Fig. 6.2(e) shows the sheet resistance (R_s) as a function of V_G at 210 K of the three devices. As expected, the gate tuning effect on R_s decreases as the LaAlO_3 thickness increases. Above $V_G = 1.5$ V, R_s almost saturates in all of the devices. We find that the gate voltage sweeps are nicely reproducible, which allows us to exclude any possible electrochemical reaction occurring on LaAlO_3 surface [94]. The forward and backward sweeps are also reversible, indicating that no electron trapping is induced in the top-gate configuration.

6.3. Tuning of Kondo effect

First, we present the temperature dependence of R_s measured under various values of V_G . Fig. 6.3(a) shows the data of device 4uc. At $V_G = 0$ V, R_s first decreases from 150 K to 10 K and then remains unchanged. In the negative voltage regime, R_s decreases monotonously to 3 K, but in the positive voltage regime, R_s first reaches a minimum at ~ 30 K and then increases as temperature decreases to 3 K. As shown in Fig. 6.3(b) and 6.3(c), the resistance minimum is always present for devices 8uc and 12uc. For a better view, the resistance relative to its value at 3 K, $R_s(T) - R_s(3 \text{ K})$, is plotted in Fig. 6.3(d)-(f). In earlier reports, this resistance upturn has been attributed to either a weak localization (WL) effect [71, 182] or a Kondo effect [70, 183]. We observed positive magnetoresistance

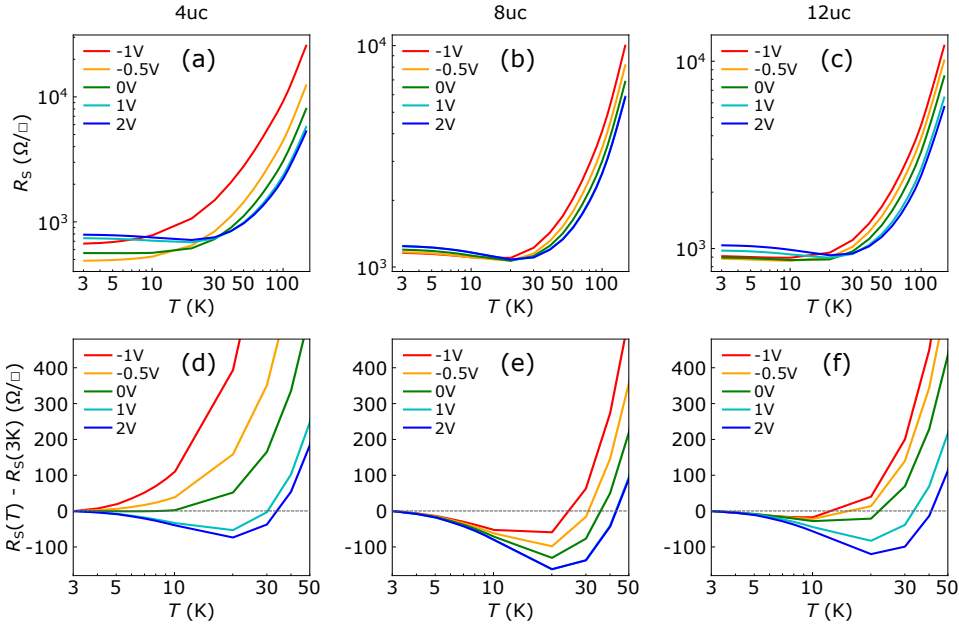


Figure 6.3: (a)-(c) Sheet resistance (R_s) as a function of temperature at various gate voltages of devices (a) 4uc, (b) 8uc and (c) 12uc. (d)-(f) Corresponding R_s relative to its value at 3 K, $R_s(T) - R_s(3K)$ of the three devices.

(MR) with sharp cusps in low magnetic fields at 3 K in all of the devices as shown in the supplemental material (Fig. 6.8, 6.9 and 6.11). The sharp cusps in low magnetic fields are characteristic features of a weak antilocalization (WAL) effect (see also Chapter 5) [72, 171] and allows us to exclude the WL effect.

In a metallic system where itinerant electrons couple antiferromagnetically with localized moments, spin-flip scattering gives rise to a resistance minimum, which is known as the Kondo effect [184]. The Kondo effect is characterized by a Kondo temperature, T_K . For $T < T_K$, the resistance increases logarithmically and eventually saturates at low temperatures. The $R_s(T)$ can be described by a simple formula [183]

$$R(T) = R_0 + aT^2 + bT^5 + R_K(T/T_K), \quad (6.1)$$

where R_0 is the residual resistance, and the T^2 and T^5 terms represent the temperature-dependent electron-electron and electron-phonon interactions, respectively. $R_K(T/T_K)$ is a universal resistivity function with the empirical form

$$R_K(T/T_K) = R_K(0K) \left(\frac{1}{1 + (2^{1/s} - 1)(T/T_K)^2} \right)^s, \quad (6.2)$$

where $R_K(0K)$ is the Kondo resistance at zero temperature and $s = 0.225$. Fig. 6.4(a)

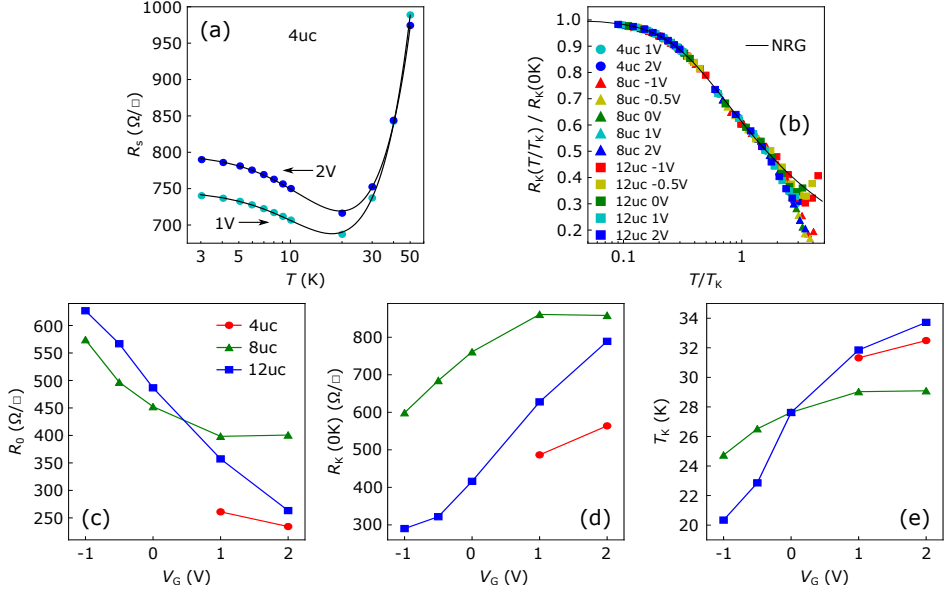


Figure 6.4: (a) R_K minimum observed from 3 to 50 K of device 4uc at 1 V and 2 V. The black lines are the Kondo effect fits using Eqs. (6.1) and (6.2). (b) Normalized Kondo resistance ($R_K(T/T_K)/R_K(0K)$) versus reduced temperature (T/T_K) curves of the three devices collapse into a single black line, which is obtained from the numerical renormalization group (NRG) method. (c)-(e) Extracted Kondo parameters, (d) the residual resistance (R_0), (e) the Kondo resistance at zero temperature ($R_K(0K)$) and (f) the Kondo temperature (T_K), as a function of V_G of the three devices.

shows the fitting results of device 4uc at $V_G = 1$ V and 2 V. The extracted values of R_0 , $R_K(0K)$ and T_K as a function of V_G for the three devices are plotted in Fig. 6.4(c)-(e).

Numerical renormalization group (NRG) method normalizes the Kondo contribution to the transport by a universal parameter T/T_K [185]. It is often used as a criterion to verify the Kondo scenario. As shown in Fig. 6.4(b), $R_K(T/T_K)/R_K(0K)$ as a function of T/T_K measured under various V_G s of the three devices all collapse into a single curve, which confirms that the Kondo effect is the origin of the observed resistance minimum. As can be seen from Fig. 6.4(d)-(e) in particular, $R_K(0K)$ and T_K are a function of the gate voltage. Such a gate-tunable Kondo effect has been previously observed in undoped SrTiO_3 single crystals [183], $\text{LaAlO}_3/\text{SrTiO}_3$ [70] and $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$ [186] EDLTs, and is consistent with our results. It is noteworthy to mention that this Kondo effect is caused by the interactions between itinerant electrons and localized electrons [183] rather than with conventional magnetic impurities, such as iron. In the presence of magnetic impurities, one would expect to observe a stronger Kondo effect at a lower carrier density, while here the gate voltage increases the carrier density.

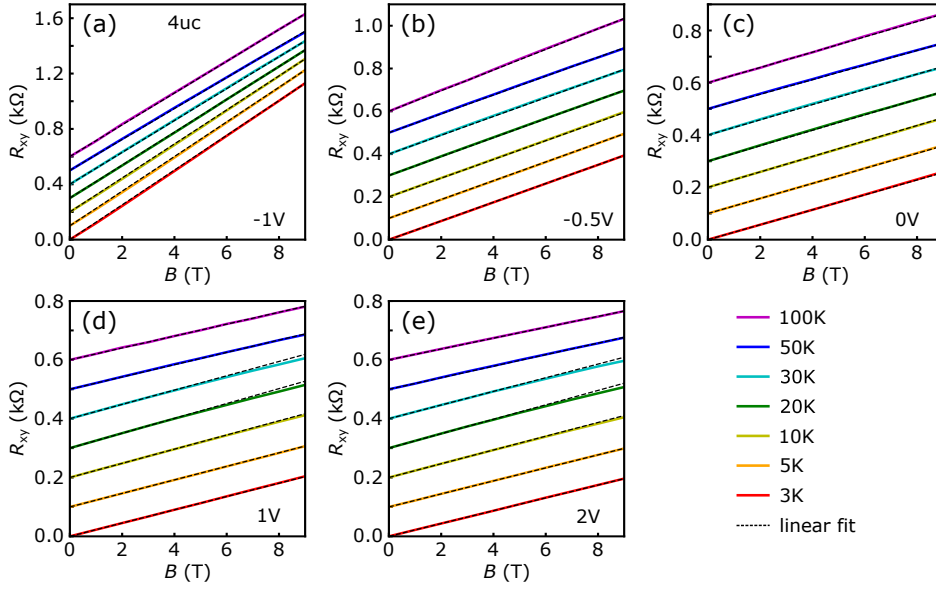


Figure 6.5: Hall resistance (R_{xy}) of device 4uc measured at various temperatures and under various gate voltages. The curves are separated by an offset of 100 Ω for clarity. The dotted lines are linear fits to $R_{xy}(B)$.

6.4. Tuning of anomalous Hall effect

Next, we present the temperature-dependent nonlinearity of the Hall resistance (R_{xy}) measured under various V_G s. Fig. 6.5 shows the data of device 4uc. The $R_{xy}(B)$ curves are separated by an offset of 100 Ω for clarity and the dotted lines are their linear fits. For the cases of $V_G = -1V$, $-0.5V$ and $0V$ as shown in Fig. 6.5(a)-(c), the $R_{xy}(B)$ curves are linear at all temperatures. For the other cases as shown in Fig. 6.5(d)-(e), the $R_{xy}(B)$ curves are linear at high temperatures (above 50 K) and low temperatures (below 10 K), but nonlinear at intermediate temperatures. For devices 8uc and 12uc, the nonlinear $R_{xy}(B)$ curves are observed at all V_G s (see supplemental material, Fig. 6.10 and 6.12). We find that the emergence of nonlinear $R_{xy}(B)$ is always accompanied by the observation of the Kondo effect.

One possibility for a nonlinear Hall effect is two-band transport [63, 89]. The band structure of the $\text{LaAlO}_3/\text{SrTiO}_3$ interface is formed by the Ti t_{2g} orbitals. For LaAlO_3 films grown on SrTiO_3 (001) substrates, the d_{xy} band stays below the $d_{xz,yz}$ bands in energy, as shown in Fig. 5.1 [61, 89, 124]. In the one-band regime, only the d_{xy} band is populated. The carrier density (n_s) and mobility (μ) can be determined by $n_s = B/eR_{xy}$ and $\mu = R_{xy}/BR_s(B=0)$, where e is the electron charge. Tuning the Fermi level to above the bottom of the $d_{xz,yz}$ bands triggers a Lifshitz transition, resulting in a nonlinear $R_{xy}(B)$.

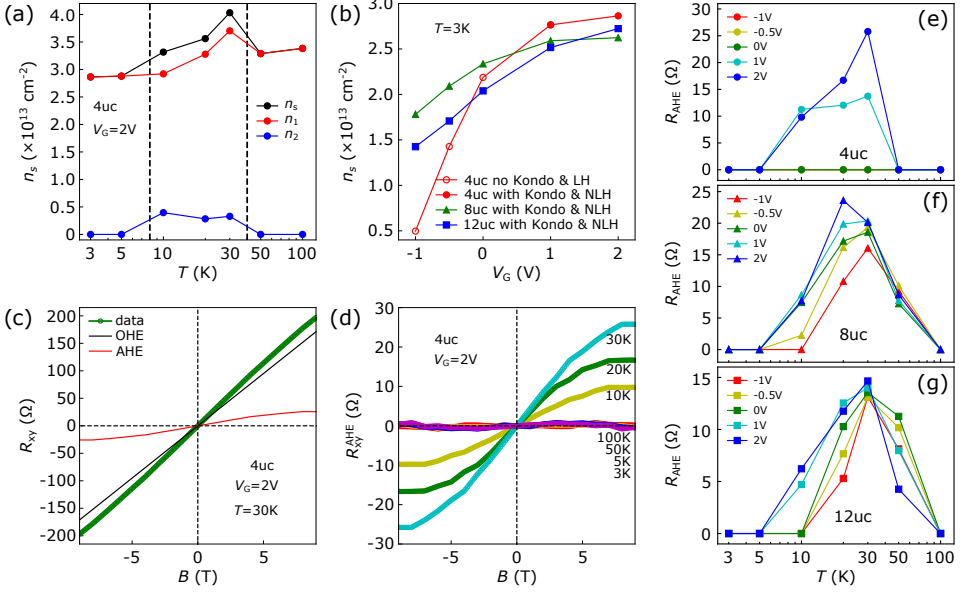


Figure 6.6: (a) Temperature dependence of the carrier density (n_s) of device 4uc at $V_G = 2\text{V}$. The values are extracted by fitting the magnetotransport data with a two-band model. n_1 and n_2 represent the carrier densities of different conduction channels and their sum is n_s . (b) n_s as a function of V_G of the three devices at 3 K. Open symbols represent no observation of Kondo effect and linear Hall (LH) effect at intermediate temperatures and solid symbols represent the observation of Kondo effect and nonlinear Hall (NLH) effect at intermediate temperatures. (c) An example for the determination of OHE and AHE terms from R_{xy} measured on device 4uc at 30 K and $V_G = 2\text{V}$. (d) Deduced AHE as a function of magnetic field at various temperatures of device 4uc at $V_G = 2\text{V}$. (e)-(g) Anomalous Hall resistance (R_{AHE}) as a function of temperature at various V_G s of devices (e) 4uc (f) 8uc and (g) 12uc.

In the two-band regime, the carrier densities and mobilities can be extracted by fitting the magnetotransport data with a two-band model [128]

$$R_s = \frac{1}{e} \cdot \frac{\frac{n_1 \mu_1}{1 + (\mu_1 B)^2} + \frac{n_2 \mu_2}{1 + (\mu_2 B)^2}}{\left(\frac{n_1 \mu_1}{1 + (\mu_1 B)^2} + \frac{n_2 \mu_2}{1 + (\mu_2 B)^2} \right)^2 + \left(\frac{n_1 \mu_1^2 B}{1 + (\mu_1 B)^2} + \frac{n_2 \mu_2^2 B}{1 + (\mu_2 B)^2} \right)^2}, \quad (6.3)$$

$$R_{xy} = \frac{B}{e} \frac{\frac{n_1 \mu_1^2}{1 + \mu_1^2 B^2} + \frac{n_2 \mu_2^2}{1 + \mu_2^2 B^2}}{\left(\frac{n_1 \mu_1}{1 + \mu_1^2 B^2} + \frac{n_2 \mu_2}{1 + \mu_2^2 B^2} \right)^2 + \left(\frac{n_1 \mu_1^2 B}{1 + \mu_1^2 B^2} + \frac{n_2 \mu_2^2 B}{1 + \mu_2^2 B^2} \right)^2}, \quad (6.4)$$

where n_1 and n_2 are the carrier densities of the first and second conduction bands, respectively, and μ_1 and μ_2 are the corresponding mobilities. For a reliable convergence n_2 and μ_2 are set to 0 in the one-band transport regime. We note that n_1 has a d_{xy} character and n_2 has a $d_{xz,yz}$ character.

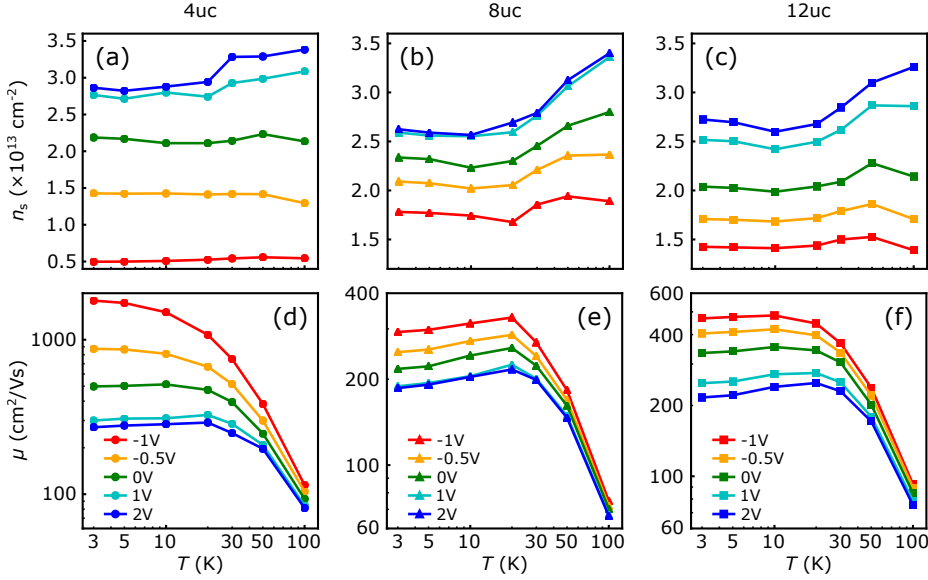


Figure 6.7: Temperature dependence of (a)-(c) carrier density (n_s) and (d)-(f) mobility (μ) of the three devices measured under various gate voltages. The values are obtained by fitting R_{xy}^{OHE} .

Fig. 6.6(a) plots the carrier density as a function of temperature of device 4uc at $V_G = 2 \text{ V}$ as an example. It can be seen that the total carrier density ($n_s = n_1 + n_2$) is $2.86 \times 10^{13} \text{ cm}^{-2}$ at 3 K and increases to $4.03 \times 10^{13} \text{ cm}^{-2}$ at 30 K, corresponding to an increase of $\sim 41\%$. In earlier reports, such a nonlinear Hall effect at intermediate temperatures has been only reported in a 26 uc $\text{LaAlO}_3/\text{SrTiO}_3$ sample [187], where the occupation of the $d_{xz,yz}$ bands has been attributed to thermally excited electrons. However, we argue that two-band conduction cannot serve as a convincing explanation for our results. First, when the 2DES enters the nonlinear regime, we obtain a large increase of n_s , ranging from 22 % to 41 %, in our three devices at various V_G s. But in Ref. [187], the increase is only $\sim 3\%$, which is much less than our case. Second, for the cases of device 4uc at $V_G = -1 \text{ V}$, -0.5 V and 0 V , we find that n_s remains almost constant at all temperatures. If thermal excitation indeed gives rise to additional electrons, one would expect to observe an increase of n_s under all V_G s. Third, in earlier reports, the critical carrier density (n_L) window for Lifshitz transition is $1.7\text{--}2.9 \times 10^{13} \text{ cm}^{-2}$ [63, 89]. We found a similar value in Chapter 4. Within our measurement limit, we observe linear $R_{xy}(B)$ at 3 K in all of the devices. Fig. 6.6(b) shows the extracted $n_s(3 \text{ K})$ as a function of V_G . The threshold carrier density for the emergence of Kondo effect differs among devices, but the overall trend is the same. Most of the values are in the n_L window, which indicates that a higher magnetic field is required to reliably analyze the transport regime and find

the expected two-band behavior. Taken together, the data at 3 K appear to preclude a two-band explanation for the nonlinear Hall effect at intermediate temperatures.

An alternative possibility for the nonlinear Hall effect is the anomalous Hall effect (AHE), which occurs in solids with ferromagnetic order [188]. In a system with AHE, R_{xy} consists of the ordinary Hall effect (OHE) term and the AHE term. As shown in Fig. 6.6(c) for the 4uc device at 30 K, the OHE term, R_{xy}^{OHE} , can be obtained from a linear fit to the high field limit of R_{xy} . Subtracting R_{xy}^{OHE} from R_{xy} will give the AHE term, R_{xy}^{AHE} [189]. Fig. 6.6(d) shows the R_{xy}^{AHE} contributions obtained at various temperatures for device 4uc at $V_G = 2$ V. Similar to common observations in the $\text{LaAlO}_3/\text{SrTiO}_3$ system, the R_{xy}^{AHE} curves show no hysteresis. Gunkel *et al.* [114] have proposed a phenomenological Langevin-type function in the spirit of the polarization of magnetic moments to describe R_{xy}^{AHE} . However, we could not obtain a satisfactory fit due to the lack of a clear magnetization saturation in the limited magnetic field. Christensen *et al.* [14] have recently reported a non-saturating AHE even up to 15 T. Fig. 6.6(e)-(g) show the anomalous Hall resistance (R_{AHE}) taken from the high field limit of R_{xy}^{AHE} , which increases as V_G is increasing. Similar temperature-dependent AHE effect has been reported in SrTiO_3 single crystals [190] and $\text{LaAlO}_3/\text{SrTiO}_3\text{:Fe}$ heterostructures [191]. Fig. 6.7(a)-(c) and 6.7(d)-(f) plot the n_s and μ as a function of temperature of the three devices under various V_G s. The values are obtained by fitting R_{xy}^{OHE} with a one-band model. The largest tunability is obtained from device 4uc.

6.5. Discussion

The Kondo effect originates from antiferromagnetic coupling between itinerant electrons and localized spins [184]. In our $\text{LaAlO}_3/\text{SrTiO}_3$ system, the Kondo scattering centers are localized and unpaired electrons [183]. The density of these localized electrons increases when increasing V_G . The temperature range in which AHE emerges is closely related to T_K . At low temperatures, $T \ll T_K$, the localized spins are effectively screened by the continuum states of the metal host upon forming coherent many-body singlet states [192]. A rough estimation of the energy scale, $g\mu_B B \approx k_B T_K$ ($g = 2$ is the g factor, μ_B is the Bohr magneton and k_B is the Boltzmann constant), indicates that a magnetic field of several tens of Tesla is required to break down the Kondo screening. Therefore a linear R_{xy} is observed. At high temperatures, $T \gg T_K$, the alignment of localized moments by magnetic field is countered by thermal fluctuations, resulting in a linear R_{xy} as well. At intermediate temperatures, $T \sim T_K$, ferromagnetic interactions between localized spins could give rise to a strong magnetic polarization in a magnetic field, resulting in the anomalous Hall effect. The origin of this non-hysteretic magnetization is still unclear. It appears to be due to the polarization of unpaired spins [80, 193], although spiral

magnetic ordering [194] might also be possible.

6.6. Conclusion

In summary, we have studied the effect of LaAlO_3 film thickness on the transport properties of $\text{LaAlO}_3/\text{SrTiO}_3$ EDLTs, and obtained the largest tunability in terms of carrier density and mobility in the device with 4 uc of LaAlO_3 . We have shown a gate-tunable Kondo effect which originates from localized electrons. More interestingly, we have also observed a gate-tunable anomalous Hall effect which always emerges near the Kondo temperature. Our results show that the physical properties of $\text{LaAlO}_3/\text{SrTiO}_3$ EDLTs are dominated by the intrinsic interactions, while the LaAlO_3 thickness has a secondary effect. Our experiments provide insights to understand the observed magnetism at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface and demonstrate a non-trivial tuning of magnetic interactions by ionic liquid gating, paving the way for designing novel electronic devices based on $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures.

Supplemental material

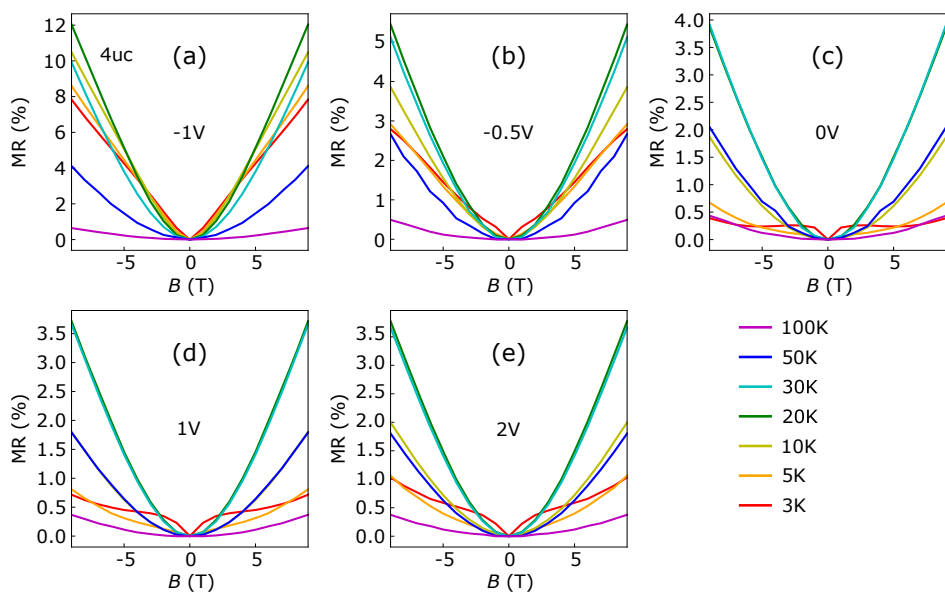


Figure 6.8: Magnetoresistance (MR) of device 4uc measured at various temperatures and under various gate voltages.

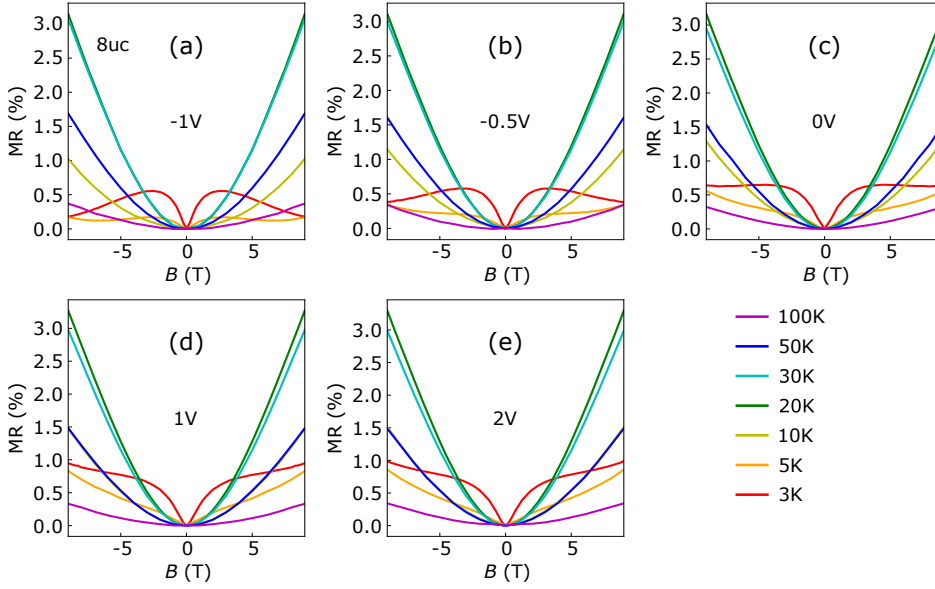


Figure 6.9: Magnetoresistance (MR) of device 8uc measured at various temperatures and under various gate voltages.

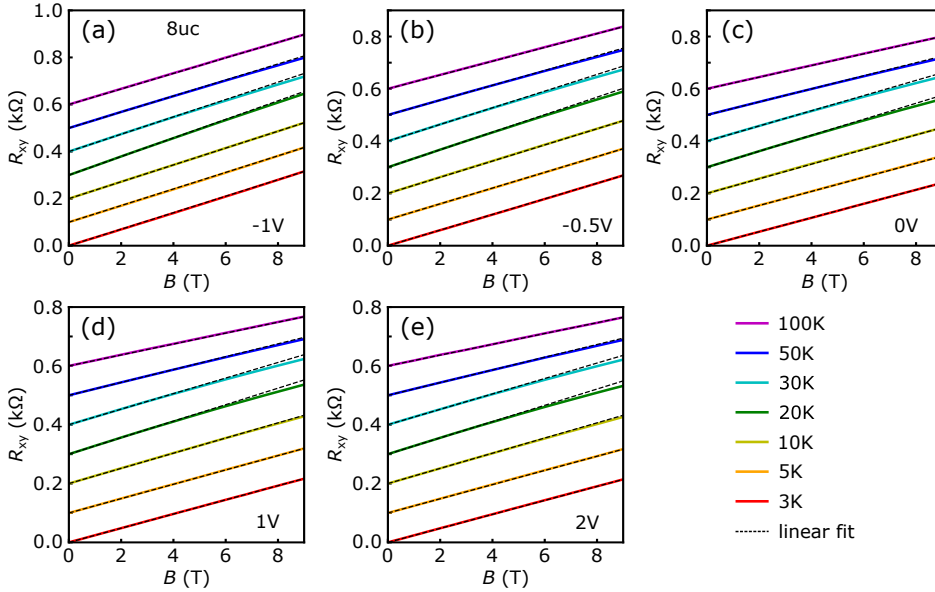


Figure 6.10: Hall resistance (R_{xy}) of device 8uc measured at various temperatures and under various gate voltages. The curves are separated by an offset of $100\ \Omega$ for clarity. The dotted lines are linear fits to $R_{xy}(B)$.

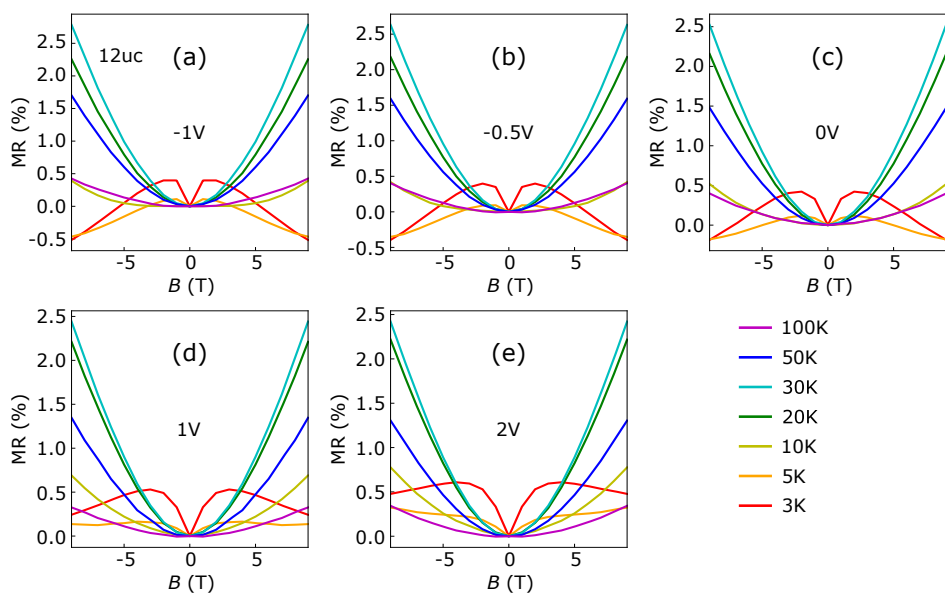


Figure 6.11: Magnetoresistance (MR) of device 12uc measured at various temperatures and under various gate voltages.

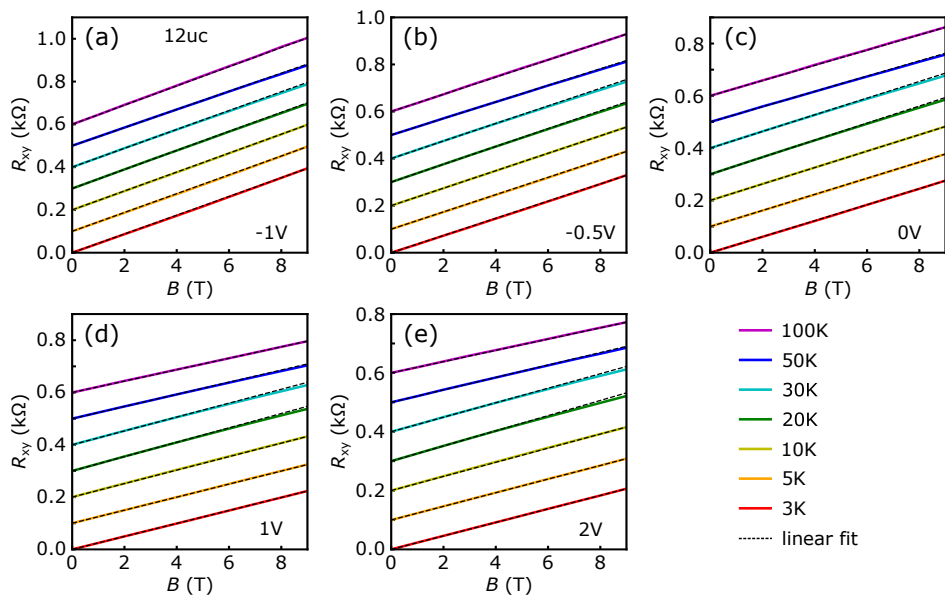


Figure 6.12: Hall resistance (R_{xy}) of device 12uc measured at various temperatures and under various gate voltages. The curves are separated by an offset of $100\ \Omega$ for clarity. The dotted lines are linear fits to $R_{xy}(B)$.

A

Self-consistent Schrödinger-Poisson calculation

A.1. Introduction

The self-consistent Schrödinger-Poisson (S-P) model was first used by F. Stern to study energy levels, populations, and charge distributions in n -type inversion layers on p -type Si in 1972 [133]. It has also been used by several groups to provide valuable insights into experimental results in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures [89, 90, 128, 132, 135].

In the S-P model, quantum effects are taken into account in the effective mass approximation, and the envelope wave function is assumed to vanish at the surface [133]. Compared to Si inversion layers, calculations for the $\text{LaAlO}_3/\text{SrTiO}_3$ interface are more complicated, which is due to the anisotropic effective mass of the Ti $3d$ orbitals and the field-dependent permittivity of the SrTiO_3 substrate [62, 91].

A.1.1. Anisotropic effective mass of Ti $3d$ orbitals

The LaAlO_3 film is grown on a SrTiO_3 (001) substrate, and the S-P calculation is performed along the growth direction, *i.e.* the z direction. The effective masses of the d_{xy} and $d_{xz,yz}$ subbands are anisotropic. We take the masses of the various bands as

$$\begin{aligned} m_{xy}^{x,y} &= m_l, & m_{xy}^z &= m_h; \\ m_{xz}^{x,z} &= m_l, & m_{xz}^y &= m_h; \\ m_{yz}^{y,z} &= m_l, & m_{yz}^x &= m_h, \end{aligned} \quad (\text{A.1})$$

where $m_l = 0.7m_e$ and $m_h = 14m_e$ [89, 124, 134], with m_e being the mass of a free electron.

A.1.2. Permittivity of SrTiO_3

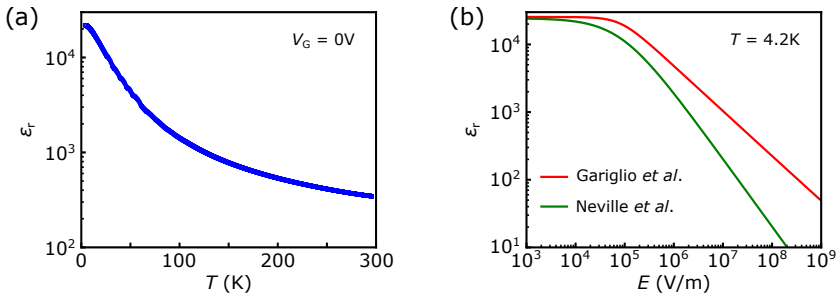


Figure A.1: (a) Temperature dependence of the permittivity (ϵ_r) of SrTiO_3 without gate voltage applied. Image adapted from Ref. [62]. (b) Electric-field dependence of ϵ_r at 4.2 K from two empirical expressions [123, 132].

SrTiO_3 single crystal has a temperature-dependent permittivity (ϵ_r) as shown in Fig. A.1(a), which reaches >20000 at low temperature. However, ϵ_r decreases when an electric

field (E) is applied to the material. So far, the field dependence of ϵ_r is still described by empirical expressions. Here, we discuss two widely used expressions. The first one was reported by Neville *et al.* [123]:

$$\epsilon_r(E) = \frac{1}{A(T) + B(T)|E|}, \quad (\text{A.2})$$

where $A(T)$ is the inverse zero-field permittivity as a function of temperature, and $B(T)$ is the field-dependent part as a function of temperature. At 4.2 K, $A = 4.097 \times 10^{-5}$ and $B = 4.907 \times 10^{-10}$ m/V for the (001) direction. The second one was reported by Gariglio *et al.* [132]:

$$\epsilon_r(E) = 1 + \frac{B}{[1 + (E/E_0)^2]^{1/3}}, \quad (\text{A.3})$$

where $B = 25462$, and $E_0 = 82213$ V/m. It can be seen from Fig. A.1(b) that the two curves overlap well in low fields but differ a lot in high fields. In $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures, the typical electric field at the interface is on the order of 10^7 V/m. Therefore, the two expressions can lead to very different results. We use Eq. (A.3) in our calculation.

A.2. Self-consistent Schrödinger-Poisson calculation

The S-P model involves the Schrödinger equation

$$\left(-\frac{\hbar^2}{2m_\alpha^z} \frac{d^2}{dz^2} + eV(z)\right) \psi_{n\alpha}(z) = \epsilon_{n\alpha} \psi_{n\alpha}(z), \quad n = 1, 2, 3, \dots, \quad (\text{A.4})$$

and the Poisson equation

$$-\frac{d}{dz} \left(\epsilon_0 \epsilon_r(E(z)) \frac{d}{dz} V(z) \right) = \rho_{3D}(z), \quad (\text{A.5})$$

where $\alpha = xy, xz, yz$ labels the Ti t_{2g} orbitals (d_{xy}, d_{xz}, d_{yz}), $V(z)$ is the confining potential, $\psi_{n\alpha}(z)$ and $\epsilon_{n\alpha}$ are normalized wave function and eigen value of the n th sub-band of the α orbital, respectively, ϵ_0 is the vacuum permittivity, and $\rho_{3D}(z)$ is the three-dimensional (3D) charge distribution.

At the $\text{LaAlO}_3/\text{SrTiO}_3$ interface, electrostatic confinement is described by the confining potential $V(z)$, which can be calculated by the Poisson equation. For a given charge distribution and electrostatic boundary conditions, $V(z)$ is uniquely defined. On the other hand, for a given $V(z)$, the distribution of mobile electrons is determined by the population of bound states in $V(z)$, which can be calculated by the Schrödinger equation. Therefore, the coupling between these two equations could enable a self-consistent calculation of $V(z)$. A schematic of the self-consistent S-P calculation is shown in Fig. A.2.

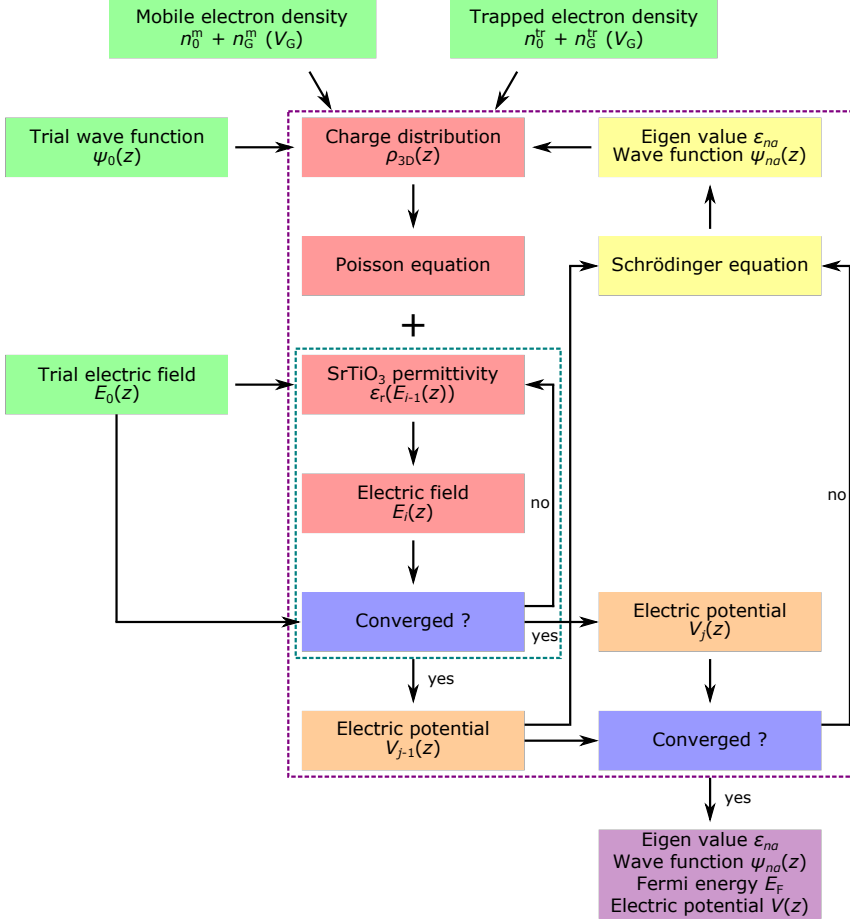


Figure A.2: Schematic of the Schrödinger-Poisson calculation, which contains two self-consistent loops. The first loop (dotted teal box) is for calculating the electric field $E(z)$ and the second loop (dotted purple box) for the electric potential $V(z)$.

A.2.1. Input parameters

Input parameters of the S-P calculation include the initial mobile electron density n_0^m , the initial trapped electron density n_0^{tr} , the gate-induced mobile electron density $n_G^m(V_G)$, the gate-induced trapped electron density $n_G^{\text{tr}}(V_G)$, a trial wave function $\psi_0(z)$, and a trial electric field $E_0(z)$. Now we discuss them one by one.

Initial mobile and trapped electron density

Initial mobile electron density n_0^m is the sheet carrier density of the virgin state, which is obtained from magnetotransport measurement. In our sample, $n_0^m = 1.41 \times 10^{13} \text{ cm}^{-2}$. Initial trapped electron density n_0^{tr} can only be obtained from trial and error until the calculated results cover the experimental results. In our case, $n_0^{\text{tr}} = 6.4 \times 10^{13} \text{ cm}^{-2}$. We take $z \geq 0$ to be SrTiO_3 and $z < 0$ to be LaAlO_3 . The positive charge density is $n_0^m + n_0^{\text{tr}}$ on the LaAlO_3 side as the boundary condition, which keeps an overall charge neutrality.

Gate-induced mobile and trapped electron density

In back-gating experiment, the total amount of electrons $n_G^{\text{tot}}(V_G)$ induced by the gate voltage (V_G) can be calculated using a parallel plate capacitor model [130, 131]:

$$n_G^{\text{tot}}(V_G) = \int_{V_1}^{V_2} \frac{\epsilon_0}{ed_{\text{STO}}} \epsilon_r(V_G) dV_G, \quad (\text{A.6})$$

where $d_{\text{STO}} = 0.5 \text{ mm}$ is the thickness of the SrTiO_3 substrate, and $E = V_G/d_{\text{STO}}$. It should be noted that the electric field E here is considered to be position independent. The reason is that E only changes significantly at the interface within about 20 nm and is constant in the SrTiO_3 bulk. As discussed in Chapter 4, the gate-induced trapped electron density $n_G^{\text{tr}}(V_G)$ can only be obtained from experimental results. In our sample,

$$n_G^{\text{tr}}(V_G) = N(1 - e^{-\frac{V_G}{400}}), \quad (\text{A.7})$$

where $N = 6.2 \times 10^{13} \text{ cm}^{-2}$. Therefore, the gate-induced mobile electron density

$$n_G^m(V_G) = n_G^{\text{tot}}(V_G) - n_G^{\text{tr}}(V_G). \quad (\text{A.8})$$

Trial wave function and trial electric field

A trial wave function ($\psi_0(z)$) gives a first guess of the mobile charge distribution. We use the Fang-Howard variational wave function, which gives a good approximation for the ground state in the z direction [131]

$$\psi_0(z) = \sqrt{\frac{b^3}{2}} z e^{-\frac{bz}{2}}, \quad (\text{A.9})$$

A

where b is the variational parameter

$$b = \left(\frac{33\pi}{2} (n_0^m + n_G^m(V_G)) a_B^2 \right)^{\frac{1}{3}} \frac{1}{a_B}, \quad (\text{A.10})$$

where a_B is the Bohr radius

$$a_B = \frac{4\pi\epsilon_r\epsilon_0\hbar^2}{m^*e^2}. \quad (\text{A.11})$$

It should be noted that the actual input values for Eq. (A.11) do not affect the final results. We take $\epsilon_r = 1$ and $m^* = m_e$.

A trial electric field ($E_0(z)$) can be any reasonable value and we take $E_0(z) = 1000 \text{ V/m}$.

A.2.2. Self-consistent calculation

First, we calculate the 3D charge distribution $\rho_{3D}(z)$, which is the sum of the distribution of mobile and trapped electrons,

$$\rho_{3D}(z) = \rho_{3D}^m(z) + \rho_{3D}^{\text{tr}}(z). \quad (\text{A.12})$$

The mobile charge distribution is given by

$$\rho_{3D}^m(z) = -e(n_0^m + n_G^m(V_G)) |\psi_0(z)|^2. \quad (\text{A.13})$$

The trapped charge distribution should also be obtained from trial and error. In our sample,

$$\rho_{3D}^{\text{tr}}(z) = \begin{cases} 0 & \text{for } z < 0 \\ -e \frac{n_0^{\text{tr}} + n_G^{\text{tr}}(V_G)}{\lambda} e^{-\frac{z}{\lambda}} & \text{for } z \geq 0 \end{cases} \quad (\text{A.14})$$

where $\lambda = 50 \text{ nm}$.

Integration of Eq. (A.5) along the z direction gives

$$-\epsilon_0\epsilon_r(E(z)) \frac{d}{dz} V(z) = -\epsilon_0\epsilon_r(E(z)) E(z) = \int_0^L \rho_{3D}(z) dz, \quad (\text{A.15})$$

where the integration range is from 0 to $L = 100 \text{ nm}$, which is divided into 2000 equal sections.

Now we enter the first self-consistent loop for calculating $E(z)$ as shown in Fig. A.2. The convergence is checked by

$$\eta = \frac{1}{L} \int_0^L \left(\frac{E_i(z) - E_{i-1}(z)}{E_i(z)} \right)^2 dz. \quad (\text{A.16})$$

If η is large than the error tolerance ϵ_p (set to 10^{-5}), a new electric field ($E'_i(z)$) is calculated by the over relaxation method in order to get a faster convergence

$$E'_i(z) = \zeta E_{i-1}(z) + (1 - \zeta) E_i(z), \quad (\text{A.17})$$

where $\zeta = 0.3$. If η is smaller than ϵ_p , the calculation is converged. Integration of $E_i(z)$ along the z direction gives the electric potential $V_{j-1}(z)$.

Next, $V_{j-1}(z)$ is injected into Eq. (A.4). The outcome of solving the Schrödinger equation is the eigen values ($\epsilon_{n\alpha}$) and the normalized wave functions ($\psi_{n\alpha}(z)$) of the subbands of different t_{2g} orbitals. We can calculate the mobile charge distribution again with $\epsilon_{n\alpha}$ and $\psi_{n\alpha}(z)$:

$$\rho_{3D}^m(z) = -e \sum_{n,\alpha} \Theta(E_F - \epsilon_{n\alpha}) \frac{\sqrt{m_\alpha^x m_\alpha^y}}{\pi \hbar^2} (E_F - \epsilon_{n\alpha}) |\psi_{n\alpha}(z)|^2, \quad (\text{A.18})$$

where Θ is the Heaviside step function and E_F is the Fermi energy. E_F can be obtained by numerically solving

$$n_0^m + n_G^m(V_G) = \sum_{n,\alpha} \Theta(E_F - \epsilon_{n\alpha}) \frac{\sqrt{m_\alpha^x m_\alpha^y}}{\pi \hbar^2} (E_F - \epsilon_{n\alpha}). \quad (\text{A.19})$$

A new $\rho_{3D}(z)$ is obtained by summing up Eq. (A.14) and Eq. (A.18).

Now we enter the larger self-consistent loop for calculating $V(z)$ as shown in Fig. A.2. By treating the new electric potential $V_j(z)$ and $V_{j-1}(z)$ with the same manner as shown in Eq. (A.16) and Eq. (A.17), a converged electric potential $V(z)$ can be obtained.

The subband dispersion can be calculated by

$$E_{n\alpha} = \frac{\hbar^2 k_x^2}{2m_\alpha^x} + \frac{\hbar^2 k_y^2}{2m_\alpha^y} + \epsilon_{n\alpha}, \quad (\text{A.20})$$

where k_x and k_y are the wavevector in the x and y directions, respectively.

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Summary

This thesis explores interfacial conductance and electric field-effects in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures. High quality epitaxial LaAlO_3 films were grown on SrTiO_3 substrates by 90° off-axis sputter deposition. The conductance properties of the interfaces were modulated by applying external electric fields in different geometries, namely back-gating (applying an electric field to the back side of the substrate) and ionic liquid gating (which applies an electric field on the side of the LaAlO_3).

Controlling the interfacial conductance in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures

In Chapter 3 we study the fabrication of conducting interfaces between LaAlO_3 and SrTiO_3 by 90° off-axis sputtering in an Ar atmosphere. At a growth pressure of 0.04 mbar the interface was metallic, with a carrier density of the order of $1 \times 10^{13} \text{ cm}^{-2}$ at a temperature of 3 K. By increasing the growth pressure, we observed an increase of the out-of-plane lattice constants of the LaAlO_3 films while the in-plane lattice constants did not change. Also, the low-temperature sheet resistance increased with increasing growth pressure, leading to an insulating interface when the growth pressure reached 0.10 mbar. We attributed the structural variations to an increase of the La/Al ratio, which also explains the transition from metallic behavior to insulating behavior of the interfaces. Our research emphasizes the key role of the cation stoichiometry of LaAlO_3 in the formation of the conducting interface, and shows that the control which is furnished by the Ar pressure makes sputtering as versatile a process as pulsed laser deposition. Compared to the latter technique, the main disadvantage of the sputtering process is that it lacks *in situ* tools to precisely control the film thickness.

Electron trapping mechanism in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures

In $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures, a commonly observed but poorly understood phenomenon is that of electron trapping in back-gating experiments. This basically means that not all charges induced by the gate are free to move and contribute to the conductance, but that some are trapped in, presumably, defects in the SrTiO_3 . In Chapter 4, by combining magnetotransport measurements and self-consistent Schrödinger-Poisson (S-P) calculations, we obtained an empirical relation between the number of trapped electrons and the gate voltage. We found that the trapped electrons follow an exponentially decaying spatial distribution away from the interface. However, contrary to earlier observations, we found that the Fermi level of the conduction band in the quantum well

remains quite far below the top of the well. The enhanced trapping of electrons induced by the gate voltage can therefore not be explained by a thermal escape mechanism, in which conduction electrons further diffuse into the substrate and get trapped. Additional gate sweeping experiments strengthened our conclusion that the thermal escape mechanism is not valid. We therefore propose a new mechanism which involves the electromigration and clustering of oxygen vacancies in SrTiO_3 . Our work indicates that such electron trapping is a universal phenomenon in SrTiO_3 -based two-dimensional electron systems. In the S-P calculation, an important ingredient is the empirical formula for the permittivity of SrTiO_3 , which depends on temperature and electric field. A thorough study of this question was performed nearly 50 years ago, but we could not obtain any reasonable description of our results using the proposed formula. Our recent study was only performed at room temperature and liquid He temperature. Therefore, it is necessary to revisit this question.

Tuning Rashba spin-orbit coupling in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures by band filling

The electric-field tunable Rashba spin-orbit coupling at the conducting $\text{LaAlO}_3/\text{SrTiO}_3$ interface has potential applications in spintronic devices, in which the electrical functions (partly) depend on the spin of the electron. However, different gate-voltage dependence of the coupling strength has been reported in experiments. On the theoretical side, it has been predicted that the largest Rashba effect appears when the Fermi level lies around the crossing point of the d_{xy} and $d_{xz,yz}$ orbitals or bands. In Chapter 5, we studied the tunability of the Rashba effect in $\text{LaAlO}_3/\text{SrTiO}_3$ by means of back-gating. By changing the back-gate voltage we can cross from a single band (d_{xy} only) to a two-band situation, which is called a Lifshitz transition. We trigger the Lifshitz transition multiple times by tuning the gate voltage so that the Fermi energy is varied to go across the band crossing between the d_{xy} and $d_{xz,yz}$ bands. By analyzing the observed weak antilocalization of the magnetoresistance, we are able to show that the maximum spin-orbit coupling effect occurs when the Fermi energy was near the Lifshitz point. Moreover, we found strong evidence for a single spin winding over the Fermi surface. Currently, the theoretical models for analyzing weak antilocalization are all based on single-band conduction. Therefore, it is very important that theorists develop new models which take multi-band conduction into account.

Tunable magnetic interactions in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures by ionic liquid gating

An electric dipole layer effect using ionic liquids is able to achieve a charge transfer orders of magnitude larger than conventional field-effect transistors. However, the large ions at the liquid-solid interface inevitably cause Coulomb scattering, which limits the carrier mobility enhancement. In Chapter 6, we study the effect of LaAlO_3 thickness on

the electrical transport properties in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures by ionic liquid gating. We find that, in our case of not too high mobilities, the interface conductance is dominated by the strong interfacial interactions rather than by the ions of the liquid. We observe a Kondo effect, which is enhanced while increasing the gate voltage. We also observe a gate-tunable and temperature-dependent anomalous Hall effect, which emerges near the Kondo temperature. Our experiments pave a way to manipulate the novel magnetic interactions in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures.

Samenvatting

Het onderzoek beschreven in dit proefschrift gaat over het optreden van geleiding en de effecten van elektrische velden aan het grensvlak tussen de materialen LaAlO_3 en SrTiO_3 . Hiervoor werden dunne lagen LaAlO_3 van hoge kwaliteit gegroeid op SrTiO_3 substraten, door middel van 90° 'off-axis' sputter depositie. Voor het moduleren van grensvlakgeleiding met elektrische velden werden twee geometrieën gebruikt, namelijk een 'back-gate' (via het aanleggen van een spanning op de achterkant van het substraat) of met een ionische vloeistof (wat een spanning aan de kant van het LaAlO_3 aanlegt).

De grensvlakgeleiding in $\text{LaAlO}_3/\text{SrTiO}_3$ dubbellagen onder controle gebracht

In hoofdstuk 3 wordt de fabricage van geleidende grenslagen tussen LaAlO_3 en SrTiO_3 bestudeerd door middel van 90° off-axis sputteren in een Ar atmosfeer. Bij groei in een druk van 0.04 mbar was het grensvlak metallisch, met een ladingdrager dichtheid van de orde van $1 \times 10^{13} \text{ cm}^{-2}$ bij een temperatuur van 3 K. Met toenemende druk vonden we een toename van de uit-vlak roosterparameter van de dunne LaAlO_3 lagen, terwijl de in-vlak roosterparameters niet veranderden. Ook ging de grensvlakweerstand bij lage temperaturen omhoog met toenemende sputterdruk, wat leidde tot een isolerende grenslaag boven een druk van 0.10 mbar. We schrijven de structuurvariatie toe aan een verandering van de verhouding La/Al, wat ook de overgang van een geleidend naar een niet geleidend grensvlak verklaart. Ons onderzoek benadrukt de sleutelrol van de cation stoichiometrie van het LaAlO_3 bij de vorming van het geleidende grensvlak, en laat zien dat de controle over de geleiding via de Ar druk het sputterproces net zo bruikbaar maakt als gepulste laserdepositie. Het voornaamste nadeel van het sputterproces in vergelijking met laserdepositie is dat er geen in situ meetmethode voorhanden is om de laagdikte met grote precisie te controleren.

Electron vangst mechanismen in $\text{LaAlO}_3/\text{SrTiO}_3$ dubbellaags structuren

Een vaak waargenomen, maar slecht begrepen fenomeen in het bestuderen van $\text{LaAlO}_3/\text{SrTiO}_3$ dubbellaags structuren is dat van electron vangst in back-gate experimenten. Dit betekent dat niet alle electronen die geïnduceerd zijn door de gate ook aan de geleiding deel gaan nemen, maar dat een aantal ervan door, waarschijnlijk, defecten in het SrTiO_3 ingevangen worden. In Hoofdstuk 4 wordt een empirische relatie verkregen tussen het aantal ingevangen electronen en de gate spanning, door het combineren van gegevens uit magnetotransport metingen en berekeningen met behulp van de zelf-consistente

Schrödinger-Poisson (S-P) vergelijkingen. We vinden hiermee dat het aantal ingevangen electronen exponentieel afneemt met toenemende afstand van het grensvlak. Anders dan bij eerdere waarnemingen echter, vinden we dat het Fermi niveau van de geleidingsband in de quantum put ver onder de bovenkant van de put blijft. Het versterkt invangen van electronen door een gate spanning kan daardoor niet verklaard worden met een thermisch ontsnappingsmechanisme, waarin geleidingselectronen verder het substraat in diffunderen en gevangen raken. Verdere experimenten waarin de gate spanning omhoog en weer omlaag gebracht wordt, versterken de conclusie dat het thermisch ontsnappingsmechanisme niet valide is. We stellen daarom een ander mechanisme voor, waarin electromigratie en het clusteren van zuurstof vacatures in het SrTiO_3 een rol speelt. Ons werk wijst er op dat electron vangst een universeel fenomeen is in dubbellaags structuren gebaseerd op SrTiO_3 . Een belangrijke ingrediënt in de S-P berekeningen is de empirische formule voor de permittiviteit van het SrTiO_3 , die afhankelijk is van zowel temperatuur als elektrisch veld. Het gedrag van de permittiviteit werd al bijna 50 jaar geleden bestudeerd, maar de formule die destijds werd voorgesteld leidt niet tot een redelijke beschrijving van onze resultaten. Onze studie beperkte zich tot kamertemperatuur en vloeibaar-Helium temperatuur, maar het lijkt nodig de vraag van het gedrag van de permittiviteit opnieuw te bekijken.

Rashba spin-baan koppeling variaties in $\text{LaAlO}_3/\text{SrTiO}_3$ dubbellaag structuren door band vulling

De Rashba spin-baan koppeling die optreedt aan het geleidende grensvlak tussen SrTiO_3 en LaAlO_3 kan beïnvloed worden door een elektrisch veld, wat tot mogelijk toepassingen leidt voor 'spintronische' schakelingen, waarin de elektrische werking (deels) van de electron spin afhangt. Eerdere studies rapporteerden verschillende afhankelijkheden van de gate spanning op de koppelingssterkte. Theoretisch werd voorspeld dat het grootste Rashba effect op zou treden als het Fermi niveau in de buurt ligt van het kruispunt tussen de d_{xy} en de $d_{xz,yz}$ orbitals of banden. In Hoofdstuk 5 hebben we dit onderzocht door het Fermi niveau te variëren met een back gate. Hierdoor kunnen we over gaan van een 1-band systeem (alleen de d_{xy} band) naar een 2-band systeem, de zogenaamde Lifshitz overgang. In het experiment gaan we verschillende keren heen en weer door de Lifshitz overgang, door de gate spanning te variëren rond het kruispunt van de d_{xy} en de $d_{xz,yz}$ banden. Door de waargenomen zwakke antilocalisatie in het gedrag van de magnetoweerstand te analyseren kunnen we laten zien dat het maximale spin-baan koppelingseffect optreedt wanneer de Fermi energie in de buurt ligt van het Lifshitz punt. We vinden ook sterke aanwijzingen voor een enkele draaiing van de spin over het Fermi oppervlak. Op dit moment zijn alle theoretische modellen voor deze analyse gebaseerd op één-band geleiding. Het is voor dit probleem belangrijk dat theoretici een meerbands

model ontwikkelen.

Verstembare magnetische wisselwerkingen in $\text{LaAlO}_3/\text{SrTiO}_3$ dubbellaag structuren met behulp van ionische vloeistoffen

Door gebruik te maken van de elektrische dipool laag in een ionische vloeistof kan een ladingsoverdracht bewerkstelligd worden die ordegrottes hoger is dan in conventionele veld-effect transistoren. De grote geladen ionen aan het vloeistof-vaste stof grens-vlak veroorzaken ook onvermijdelijke Coulomb verstrooiing, waardoor de toename van de mobiliteit van de ladingsdragers beperkt wordt. In Hoofdstuk 6 bestuderen we het effect van de dikte van een LaAlO_3 laag op de elektrische-transport eigenschappen van $\text{LaAlO}_3/\text{SrTiO}_3$ dubbellagen als daar een ionische vloeistof gate op wordt aangebracht. We vinden dat, in ons geval van niet al te hoge mobiliteiten, de grensvlakgeleiding gedomineerd wordt door de interacties in de grenslaag, en niet zozeer door de ionen in de vloeistof.

List of Publications

- **C. Yin**, D. Krishnan, N. Gauquelin, J. Verbeeck, and J. Aarts. Controlling the interfacial conductance in $\text{LaAlO}_3/\text{SrTiO}_3$ in 90° off-axis sputter deposition, *Physical Review Materials*, **3**, 034002 (2019).
- **C. Yin**, A. E. M. Smink, I. Leermakers, L. M. K. Tang, N. Lebedev, U. Zeitler, W. van der Wiel, H. Hilgenkamp, and J. Aarts. Electron trapping mechanism in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures, *under review*.
- **C. Yin**, P. Seiler, L. M. K. Tang, I. Leermakers, N. Lebedev, U. Zeitler, and J. Aarts. Tuning Rashba spin-orbit coupling in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures by band filling, *under review*.
- **C. Yin**, K. Prateek, W. Gelling, and J. Aarts. Tunable magnetic interactions in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures by ionic liquid gating, *under review*.
- J. Jobst, L. M. Boers, **C. Yin**, J. Aarts, R. M. Tromp, and S. J. van der Molen, Quantifying work function differences using low-energy electron microscopy: The case of mixed-terminated strontium titanate, *Ultramicroscopy*, **200**, 43–49 (2019).
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Curriculum Vitæ

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