Two-dimensional transport in oxide heterostructures

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**NANYANG
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UNIVERSITY**

**TWO-DIMENSIONAL TRANSPORT IN OXIDE
HETEROSTRUCTURES**

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**TWO-DIMENSIONAL TRANSPORT IN OXIDE
HETEROSTRUCTURES**

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Summary

The entanglement of charge, spin, orbital and even lattice degrees of freedom in transition metal oxides gives rise to a wide spectrum of exotic properties, like high transition temperature superconductivity and colossal magnetoresistance. The interfaces between these exotic transition metal oxides offer an even more tantalizing platform for the study not only on the fundamental science, but also on potential applications. The $\text{LaAlO}_3/\text{SrTiO}_3$ (LAO/STO) heterostructure is one of the prototypical cases, which exhibits two-dimensional conduction and rich physical properties although both LAO and STO are *insulating in bulk form*. In this thesis, I will present my exploration on the transport properties of such oxide heterostructures synthesized with unit-cell precision.

In my first project, I carried out electric field effect experiments on the LAO/STO heterointerface using the electric double layer transistor (EDLT) structure, through which a metallic behavior was achieved at the insulating three unit cell (uc) LAO/STO heterointerface. By examining the relationship between the conductance and carrier density at the heterointerface, we found that the insulator-to-metal transition exhibited a percolative nature. The percolation property is attributed to the unscreened inhomogeneous potential at the LAO/STO interface when the carrier density is low, which is also in line with the observed giant linear positive MR. In the high gate voltages regime, where the carrier concentration is above $\sim 1.69 \times 10^{13} \text{ cm}^{-2}$, Kondo effect was found, manifested by the resistance upturn and the

characteristic magnetotransport behavior at low temperatures. The strength of the Kondo coupling between the localized spins and the itinerant electrons was quantitatively analyzed by using the numerical general method and fitting to the weak antilocalization model.

Next I will demonstrate the tuning of the spin-orbit interaction (SOI) in the termination-resolved asymmetric LAO/STO/LAO heterostructures by adjusting the thickness of the inserted STO layer. The SOI was manifested by the observation of the weak antilocalization effect in the magneto-transport measurements. The Rashba SOI parameters evolving with the STO thickness were obtained through model fitting, and the discovery of electrostrictive effect revealed the concurrence of the built-in electric field in the STO layer.

The projects I carried out during my PhD study were enabled by the advance of the most state-of-the-art synthesis technique to produce unit-cell-controlled oxide heterostructures. In the field effect experiment on LAO/STO interfaces, charges orbitals and spins as well as their correlations collectively dictate the overall transport through symmetry breaking and spin-related scattering. The lattice degree of freedom further proves to be an important factor in the transport of asymmetric LAO/STO/LAO heterostructures with strong electrostriction effect. The rich physics and versatile functionalities underscore such ultrathin oxide heterostructures as promising candidates for future oxide electronics.

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List of Abbreviations

R	Resistance	BIA	Bulk inversion asymmetry
ρ	Resistivity	SIA	Structure inversion asymmetry
σ	Conductance	ILP	Iordanskii-Lyanda-Geller-Pikus model
I	Current	HLN	Hikami-Larkin-Nagaoka model
V	Voltage	BKT	Berezinskii-Kosterlitz-Thouless model
V_g	Gate voltage	2DEG	2 dimensional electron gas
V_c	Critical gate voltage	2DEL	2 dimensional electron liquid
Ω	Ohms	SXRD	Surface X-ray diffraction
n	Carrier density	TEM	Transmission electron microscopy
μ	Mobility	PLD	Pulsed laser deposition
m_e	Bare electron mass	RHEED	Reflection high energy electron diffraction
m^*	Effective electron mass		
T	Temperature	AFM	Atomic force microscopy
T_K	Kondo temperature	XRD	X-ray diffraction
h	Planck constant	BHF	Ammonium fluoride buffered HF
uc	Unit cell	CVD	Chemical vapor deposition
C_g	Area capacitance	PVD	Physical vapor deposition
T	Tesla	MBE	Molecular beam epitaxy
MR	Magnetoresistance	XRR	X-ray reflectivity
B	Magnetic field	RSM	Reciprocal space mapping
l_ϕ	Phase coherence length	STM	Scanning tunneling microscopy
τ_0	Elastic lifetime	PPMS	Physical properties measurement system
$\text{\AA}$	Angstrom	EDLT	Electric double layer transistor
J	Exchange interaction		
Ψ	Digamma function		
E	Electric field		
v	Velocity		
c	Speed of light		
σ	Pauli spin matrices		
μ_B	Bohr magneton		
L	Orbital angular momentum		
S	Spin angular momentum		
k	Wave vector		
p	Electron momentum		
e_z	Unit vector		
P	Polarization		
$T_{\min}$	Minimum resistance temperature		
NRG	Numerical renormalization group		
WL	Weak localization effect		
WAL	Weak anti-localization effect		
SOI	Spin orbit interaction		

List of Publications

- [1] **W. Lin**, J. Ding, S. Wu, Y. Li, J. Lourembam, S. R. Shannigrahi, S. Wang and T. Wu, "Electrostatic Modulation of $\text{LaAlO}_3/\text{SrTiO}_3$ Interface Transport in an Electric Double-Layer Transistor", *Adv. Mater. Interfaces* **1**, 1300001 (2014).
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Chapter 1

Introduction

1.1 Background and introduction

Human's modern life should thank the invention of the transistors, which underlies the the developments of electronics, telecommunication and many cutting-edge technologies in our society. Transistors are operated based on the charge modulation, i.e. turning on/off (logical “1”/“0”) current in the channel by the electric field. Though semiconductor silicon (Si) is the key component of the transistors, according to the classical band model, its functionality mainly rely on the interface with dielectric insulator, not on the bulk. Moreover, this kind of interface between certain semiconductor and insulator can be further functionalized to introduce quantum transport phenomena, such as integral and fractional quantum hall effects [1]. These exotic physical phenomena as well as the practical applications make the Si and other similar semiconductors, like Ge and InAs, one of most successful science “stories” in scientific history.

The semiconductors are band insulator, where there are no interactions between electrons and hence less excited physical properties are present in bulk. In contrast, there are other kinds of materials in which the electron interaction matters. Transition metal oxide is one of these novel materials. In such complex materials, in addition to the charge degree of freedom, which dominates the physical properties in

semiconductors, the spin, orbital and lattice degrees of freedom may entangle themselves with one another and, as a result, give rise to many spectacular physical properties in bulk samples, such as high temperature superconductivity, colossal magnetoresistance, multiferroic, etc [2-3]. Since these transition metal oxides have similar structures, many of them can also be stacked together with well-defined interface, which creates great opportunities to explore potentially novel devices and/or physical properties. Thanks to the recent developments of the state-of-the-art growth equipments, including pulsed laser deposition (PLD) and molecular beam epitaxy (MBE), intense efforts have been made to explore the rich physics of transition metal oxides and some exotic results have been achieved in the past decades.

In this thesis, I studied the two dimensional transport of the oxide heterointerfaces between prototypical transition metal oxide SrTiO_3 (STO) and LaAlO_3 (LAO). Although both are electrical insulating, the interface shows two-dimensional conductivity with exotic phenomena, including superconductivity, magnetism, and even their coexistence at certain conditions [4-8]. These observed phenomena make the heterostructure stacked by the two band insulators being attractive as a novel platform not only for the exploration of fundamental physics, but also for the potential oxide electronics. In the following chapters, I will present my efforts on the exploration of two directions. In the first one, the electric double layer transistor was used to modulate the ground state of the heterointerface and to realize the two-dimensional insulator-to-metal transition. In the second one, an

alternative method was explored to control the strength of spin-orbit interaction (SOI) in asymmetric LAO/STO heterostructures.

1.2 Transition metal oxide films and heterostructures

One of the most important structures in transition metal oxides is perovskite, which has a formula of ABO_3 , where A and B are metal cations and O represents oxygen anion. The perovskite crystal structure is shown in **Fig.1.1a**. In such a structure, a transition metal ion usually occupies the B site and coordinates with surrounding oxygen anions to form the BO_6 octahedra structure, whereby the resulting crystal field splits the 3d orbitals of the transition metal cation (**Fig.1.1b** and **c**). Specifically, the ABO_3 structure can be seen as being stacked by the AO and BO_2 planes alternatively in the [001] crystallographic direction. The ideal perovskite structure is centrosymmetric simple cubic, where the bond angle of B-O-B is 180 degree. However, lower symmetry structures are preferable in most cases, especially at low temperatures, with the non-ideal ratio between A-O and B-O bond lengths (r_{A-O} and r_{B-O}). This ratio is called Goldschmidt tolerance factor, which is defined as $t = r_{A-O} / \sqrt{2}r_{B-O}$ [9]. In the ideal cases, $t = 1$. If $t > 1$, the smaller B ion will tend to move off-center, giving rise to the polar distortion, which happens in case of $BaTiO_3$ with the spontaneous polarization below Curie temperature point. Given a B cation with larger size, i.e. in case of $t < 1$, the BO_6 octahedra structure tends to have cooperative tilts or rotations while maintaining their corner-sharing connectivity, leading to the reduction of B-O-B bond angle. This situation can be found in many

magnetic oxides, whose magnetic properties are sensitive to the change of the bond angle.

Figure 1.1 Schematic structure of perovskite ABO_3 (a) and its orbital energy levels under cubic crystal field due to oxygen ions. (c) shows the five typical 3d orbitals.

Besides the displacement of B ion introduced above, the bond length can also be changed by the Jahn-Teller effect, as a result of electronic instability and hence removing the degeneracy of 3d states of B ion.

Figure 1.2 The degrees of freedom existed in transition metal oxide and the parameters used to modify the interactions among degrees of freedom in oxide heterostructure. From Ref. [9]

Accordingly, the electronic properties of the perovskites are strongly related to the bond length and B-O-B angle, which exemplifies the complex but interesting couplings between the charge, spin, orbital and lattice degrees of freedom in transition metal oxides. This in turn offers a valuable principle to find the ways to manipulate the functionalities of the oxide system. Formation of thin films offers one of such ways. The tunability is mainly obtained by the strain effect imposed by the substrates, which can distort and/or rotate the BO_6 octahedra to change the bond length and/or bond angle, which in turn exert influence on the electronic properties of the films [10], which has been actively discussed theoretically and explored in many oxide systems, such as LaTiO_3 , LaNiO_3 , SrRuO_3 , LaCoO_3 , etc. In addition, confinement and size effects may also play a role in modifying the electronic

properties of the oxide thin film when the film is thin enough. The strong correlated oxide -- SrVO_3 , for example, is one of the cases, which has been reported to exhibit metallic quantum well states in the form of ultrathin films [11].

Inspired by the concepts of semiconductor transistors and thanks to the developments of the state-of-the-art growth techniques (MBE and PLD), which make the fabrication of the artificial oxide structure with well-defined interface possible, some recent works of transition metal oxides have been devoted to the interfaces in heterostructures. This configuration offers many potential ways to purposely control the certain degrees of freedom [9,12], as shown in **Fig. 1.2**. Besides the effects discussed above, there are two extra features introduced for the electrons at interface, i.e. the enhanced electron correlation due to the low dimensionality and broken inversion symmetry [12]. In addition, the atomic-sharp interface allows certain hopping processes between orbitals of neighboring transition metal ions across the interface. Consequently, the spin and/or orbital moments at the heterointerface can be induced with the help of the coulomb interaction. As a result, the charge, orbitals and/or spin reconstructions happen in the interface between transition metal oxides, thus leading to some emergent phenomena. In the past decade, many systems with the interface reconstruction have been studied, which can be discussed according to the main degree of freedom involved [12].

- **Charge transfer.** The typical case is the $\text{LaTi}^{3+}\text{O}_3/\text{SrTi}^{4+}\text{O}_3$ heterointerface, where metallic behavior was found, while the LaTiO_3 is a Mott insulator and SrTiO_3 a band insulator [13]. Such metallic behavior is interpreted as the result

of a certain amount of charges being transferred from the Ti^{3+} to Ti^{4+} at the heterointerface. This charge transfer process can also lead to the emergent of superconductivity between the insulating La_2CuO_4 and the metallic overdoped $(\text{La,Sr})_2\text{CuO}_4$ [14], ferromagnetic metallic state between the antiferromagnetic insulator LaMnO_3 and SrMnO_3 [15], etc.

- **Electrostatic boundary condition.** This phenomenon, related to the charge transfer, normally occurs at the polar/nonpolar heterointerfaces. In such scenarios, the strong-enough accumulated potential energy in the polar layer drives the electron reconstruction at the heterointerface to avoid the “polar catastrophe”. The $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructure is one of the typical cases [16], which is also the system studied in this thesis work and will be discussed in details in the next section.
- **Spin and orbital reconstructions.** These reconstructions can come along with the charge transfer process in certain heterointerfaces because of the entanglement of charge, orbital and spin degrees of freedom [12]. They can also be induced by the tilt and/or rotation of oxygen octahedra due to the epitaxial strain in a heterostructure as discussed above [10] and, in such cases, the reconstruction extends far from interface. In contrast to the above scenarios, the local spin and/or orbital reconstruction at a heterointerface can also be directly induced by the discontinuity of local environment of transition metal ions, resulting in the enhancement or suppression of the exchange bonds of transition metal ions in the direction perpendicular to the interface [17-18].

- **Spin-orbit interaction.** The broken inversion symmetry at oxide interfaces can introduce spin-orbit interaction. This relativistic effect gives rise to an effective magnetic field, which interacts with the magnetic moment of electrons and hence may have important influences in the electronic ground state at oxide interfaces [12,19].

1.3 $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructure

1.3.1 Strontium titanate (SrTiO_3) and Lanthanum aluminate (LaAlO_3)

- **Strontium titanate (SrTiO_3)**

The SrTiO_3 (STO) crystal is a non-magnetic band insulator with an indirect band gap of ~ 3.25 eV [20]. Like the role of Si in semiconductors, STO is the workhorse in the study of oxides, especially in the field of oxide electronics. Besides being the substrate for a wide range of other functional oxides, STO also exhibits a lot of interesting properties. The stoichiometry STO is a quantum paraelectric material with a dielectric constant of over 2000 at low temperatures [21]. This giant dielectric constant contributes to the suppression of ionized impurity scattering and the low donor binding energy in semiconducting or metallic STO. Doping STO with Lanthanum (La) [22], niobium (Nb) [22-24] or oxygen vacancy [24-25] can lead to a very wide range of carrier density and high mobility at low temperatures [24]. In addition, STO can also be doped into being superconductor with dome shape behavior similar to the case of cuprates

[26-28].

Figure 1.3 The splitting of Ti 3d orbital under conditions of cubic crystal field.

These resulted orbitals can be further split by application of the compressed and tensile strain on the TiO₆ octahedra in z direction.

With the tolerance factor of ~ 0.96 , the rotation of TiO₆ octahedra structure occurs at 105 K, driving a second-order transition from the simple high temperature cubic structure to the low-temperature tetragonal phase [29-30]. Consequently, the degeneracy of six-fold t_{2g} band, resulting from the crystal field splitting, is lifted, forming a low energy t_{2g} (d_{xz}/d_{yz}) band and a high energy d_{xy} band [31], as illustrated in **Fig. 1.3**. The resulted low energy t_{2g} band can be further split by a spin-orbit interaction [31-32]. On the other hand, if the octahedra are confined in two dimensions, the lowest energy band will be d_{xy} , which has been observed by spectroscopic techniques at the surface of STO [32] and the LAO/STO heterointerface [33].

- **Lanthanum aluminate (LaAlO_3)**

LaAlO_3 (LAO) is also a non-magnetic band insulator with a large band gap of ~ 5.6 eV. In contrast to STO with neutral components, SrO and TiO_2 , along the [001] crystallographic direction, the stacking counterparts of LAO are charged ones, i.e. $(\text{LaO})^{1+}$ and $(\text{AlO}_2)^{1-}$. As a result, there is an electrostatic potential established in the ideal stacking direction, which diverges as the thickness increases if no reconstructions happen. In practical, it is normally avoided by the formation of defects on the surface of the bulk LAO [34].

1.3.2 Exotic phenomena at $\text{LaAlO}_3/\text{SrTiO}_3$ heterointerface

In this section, I will mainly describe the exotic reconstruction phenomena from the aspects of transport, orbital and lattice at the LAO/STO heterostructure, whose schematic structure is shown in **Fig. 1.4a**.

Electronic transport properties

Hwang's seminal work gave one of the defining transport features for the LAO/STO heterostructure: the termination dependence of conductivity, that is, the conductivity only come about at the LaO/TiO_2 heterointerface, not at the AlO_2/LaO counterpart [16,35], as shown in **Fig. 1.4b**. Later, it was found that the conductivity also depended on the thickness of LAO [36], which is another defining feature of the heterostructures and strongly supports the intrinsic mechanism of the conductivity, to be discussed in the next section. The threshold thickness of LAO is 4 uc, below which no carrier density can be detected and the resistance of the heterointerface is

over $M\Omega$, as shown in **Fig. 1.4c**. The further study showed that the threshold could be tuned by the strain imposed on the STO [37] or the component of the LAO capping layer [38].

Figure 1.4 The electronic transport properties of the $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructure.

(a) schematic structure of LAO/STO structure; From Ref. [36] (b) the termination dependent resistance as function of temperature; From Ref. [35] (c) The thickness of LAO layer dependence of conductance of the LAO/STO heterointerface. From Ref. [36] (d) The evidence of the coexistence of ferromagnetism and superconductivity in the heterointerface, where the blue curve shows the magnetic field dependence of

magnetic moment at 20 mK below superconducting transition temperature, while the field dependent resistance is shown in blue curve. From Ref. [6] (e) Sheet carrier density dependence of mobility in LAO/STO heterointerface (From Ref. [39]). The inset shows the Shubnikov–de Haas oscillations observed in film prepared in low temperature. From Ref. [40]

However, a thicker LAO layer cannot guarantee a better conductivity in the heterointerface, as it was reported that with thicker LAO the mobility of electrons decreased, though the carrier density increased [41-42]. Nevertheless, it is in the thicker LAO case (26 uc) where the many-body magnetic behavior was first observed at the heterointerface according to the observations of resistance upturn at low temperature and magnetoresistance hysteresis [4]. Almost at the same time, the superconductivity with transition temperature of 100-200 mK was observed at the heterointerface, though prepared at different conditions [8]. Analogue to the high- T_c cuprates, the superconductivity at the LAO/STO heterointerface exhibits dome-shape dependence of the critical temperature as well as the particular carrier dependence of pseudogap [43]. Furthermore, the superconductivity can be effectively tuned by the gate bias in a wide carrier density range with the quantum phase transition between a superconducting phase and an insulating state, which was reported to be consistent with the two dimensional Berezinskii–Kosterlitz–Thouless (BKT) behavior [44].

As a result, these controversial but interesting ground states – a magnetic state and a superconducting state - stimulated great efforts to find further insights behind them. Such efforts led to the uncommon observation of the coexistence of

magnetic state and superconductivity in the heterointerface [5-7], as shown in **Fig. 1.4d**, which is usually discussed in some heavy fermion systems [45]. Regarding the mechanism of the exotic phenomenon, electronic phase separation and intrinsic coexistence facilitated by the spin-orbit interaction in the heterointerface were proposed [46-49]. However, more efforts are required to solve, if possible, the puzzle.

In contrast to the conventional two dimensional electron gas (2DEG) at semiconductor interface, the carriers at the LAO/STO heterointerface were dubbed as the two dimensional electron liquid (2DEL) because of the electron-electron interaction [50]. This correlation partly contributes to the low mobility found in the heterointerface, which is also suppressed by the electron-phonon scattering and impurity scattering, dominating at different temperature ranges. To improve the mobility, many efforts have been done and consequently, it has been found the mobility of the 2DEL presents flexible tunability upon the external parameters. The lower growth temperature has been reported to enhance the mobility, due to unknown mechanisms, which results in the observation of two dimensional quantum oscillations in magnetoresistance measurement (inset of **Fig. 1.4e**) [40]. In addition, the mobility can also be effectively enhanced by methods of surface control [39] and/or one dimensional confinement [51].

Band structure reconstruction

In contrast to the conventional semiconductors devices, where the bands are bended to result in the accumulation/inversion of charge carriers and no reconstructions in

orbitals and/or lattices occur, the LAO/STO exhibits such reconstructions at the heterointerface. The original degenerate t_{2g} band, due to the simple cubic structure at room temperature, reconstructs into a splitting state with the d_{xy} being the lowest energy orbital and the d_{xz}/d_{yz} the higher one at the heterointerface, which is attributed to the confinement effect and confirmed by the X-ray absorption spectroscopy (XAS) measurement [33]. Recently the microscopic information of the electronic structure at the heterointerface and nearby layers was further explored via the interface-sensitive resonant photoelectron spectroscopy technique [52-53]. As shown in **Fig. 1.5**, the resulted band structure and the fitted band dispersions clearly show the splitting of the t_{2g} band of the Ti ions at the heterointerface.

Figure 1.5 The band structure near the Fermi level along Γ -X- Γ direction at the conducting LAO/STO heterointerface. The white lines represent the theoretical band dispersions. From Ref. [53]

Lattice reconstruction

As the lattice constants for STO and LAO are 3.905 Å and 3.79 Å, respectively, there is a tensile strain subjected by the epitaxial LAO film in the heterostructure. Consequently the strain effect elongates (compresses) the in-plane (out-of-plane) lattices of the LAO film. However, as this classical strain effect has only trivial effects on the electronic properties, more research interests have been focused on the local lattice reconstructions around the heterointerface experimentally and theoretically. Though there is still no consensus regarding the exact details of the reconstructions, due to the limited techniques with the local atomic-scale resolution and the variety of the heterostructures prepared under different conditions (i.e. the structure reconstructions may be sensitive to the growth temperature, oxygen background pressure and so on.), it is always a key factor to be considered for further study on the LAO/STO heterostructure.

So far there are a few kinds of lattice reconstructions observed experimentally. The first one is the polarization in the STO layers nearby the interface, which was detected by techniques of surface X-ray diffraction (SXRD) [54] and ultra-high resolution transmission electron microscopy (TEM) [55]. The polarization of the STO layers nearby the heterointerface was proposed to be caused by the polar field from the LAO layer, and it can offer an satisfactory explanation for the memory switch behavior of the devices based on the insulating 3 uc LAO/STO [56]. However, it should be noted that for some reports the polarization in STO layer nearby the interface wasn't observed, though using the same technique (SXRD) [57]. Further,

the possible oxygen octahedron reconstruction in nearby STO layers was reported too, according to which the oxygen octahedron rotation in originally cubic STO is induced by the epitaxial-grown rhombohedra LAO film [55]. Due to the strong polar field, the LAO layer in the LAO/STO heterostructure can also experience a lattice reconstruction – buckling according to the theoretical calculations [58]. Such reconstruction leads to a relatively movement between cations and anions and hence results in the polar distortion in the LAO layer, which allegedly have contribution in compensation to the diverging potential in the LAO layer. Experimentally, this distortion was indeed detected according to some studies by SXRD technique [57,59].

1.3.3 Doping mechanism

An immediate question about these exotic phenomena introduced above is their origin. So far three scenarios have been suggested to be responsible for the observed exotic phenomena, i.e. “polar catastrophe”, oxygen vacancies and cations intermixing at the heterointerface. Among these, the “polar catastrophe” scenario gives the most successful answer to most of the observed properties at the LAO/STO heterostructure, however, not completely.

In the [001] crystallography direction, LAO can be seen as being stacked by $(\text{LaO})^+$ and $(\text{AlO}_2)^-$ layers alternatively, and STO by $(\text{SrO})^0$ and $(\text{TiO}_2)^0$. Therefore, when the LAO is epitaxially grown on the STO substrate, a polar discontinuity happens at the abrupt interface between them. The discontinuity can result in the

accumulation of the electric potential in LAO layer, whose strength increases with its thickness and may eventually diverge if no reconstruction occurs to compensate the energy. In the band structure model, as shown in **Fig. 1.6**, the bands of LAO are pushed up continuously with the increase of the thickness of LAO. While in conventional semiconductor polar/nonpolar heterostructure, like Ge/GaAs, the “polar catastrophe” is avoided by the atomic reconstruction [60], the LAO/STO intends to avoid this by the electron reconstruction due to the variable valence of Ti. Accordingly, electrons from the O2p band, which locates at the maximum valence band, of the surface LAO layer will be transferred to the Ti 3d conduction band, the minimum conduction band of STO. At the interface, the internal electric field of polar LAO is quite strong, where the valence band of LAO overlaps with the conduction band of STO [61-63]. As a result, the charge transfer process leads to the occupation of the Ti 3d band by mobile carriers at the heterointerface and holes in the surface O2p band. It should be noticed that the process discussed above is the one for the n-type interface. For the p type interface, the atomic reconstruction is proposed to be the compensation mechanism, which consistently explains the observed insulating behavior at the LAO/STO interface [61].

Figure 1.6 The polar catastrophe mechanism for the conductivity in LAO/STO heterointerface. (a) and (b) show the schematic band structures of the LAO/STO structure before and after electron reconstruction, respectively, while the (c) and (d) show their charge, electric field and potential distributions in LAO layer. (a) and (b) from Ref. [63]; (c) and (d) from Ref. [61]

The “polar catastrophe” scenario elegantly explains the defining features of the LAO/STO heterostructure, i.e. the termination and thickness dependence of conductivity, which cannot be explained by the other models involving the extrinsic defects, such as oxygen vacancies and cation interdiffusion. However, there are still several discrepancies which cannot be well explained by the “polar catastrophe” scenario. The first one is the discrepancy between the carrier density at the LAO/STO heterointerface obtained by the transport measurement and the theoretical value of $\sim 3.3 \times 10^{14} \text{ cm}^{-2}$ [64], and the difference is almost one order of magnitude. The other one is the failure in detecting the internal electric field in LAO by sensitive

photo spectroscopic methods [53,65], though the internal field is reported in study with scanning tunnel technique (STM) [66].

Consequently, there are other scenarios proposed to solve these puzzles. Oxygen vacancies scenario can explain the transport properties for the structure prepared at the low oxygen pressure [67], which however, does not work for the ones prepared at high oxygen pressure and/or with post-annealing in rich oxygen environment for a long time. The interdiffusion at the heterointerface forming a bulk-like solution $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$ is proposed for the conductivity and the atomic displacement around the heterointerface [68], which, however, fails to explain the thickness dependence of conductivity. Regarding the missing internal electric field in LAO, the proposed surface defects [69] and polar distortion [58] in LAO layer may contribute to its “disappearance”, and these factors can also explain the discrepancies of the carrier densities and thus seems to be a good complementary scenario to “polar catastrophe”. However, more efforts are still required to have a comprehensive understanding on the exotic phenomena observed in the LAO/STO heterostructure.

1.3.4 Other related oxide heterostructures

As the “polar catastrophe” scenario hinges on the polar character of materials, it should also be suitable for other polar/nonpolar heterostructures. At this moment, most of the studies focus on the system with different polar materials, such as NdAlO_3 [70], PrAlO_3 [70], NdGaO_3 [70], LaVO_3 [71], GaTiO_3 [72], etc. In these systems, similar electronic properties were found. One of the remarkable examples

comes from the study on $\text{LaCrO}_3/\text{SrTiO}_3$ [73], where the built-in field was detected by X-ray photoemission spectroscopy. However, no conductivity found at the heterointerface, which was attributed to the atomic reconstruction as well as the charge redistribution inside LaCrO_2 . This offers another example for the rich varieties of phenomena at the oxide heterointerfaces and also challenges our understanding and techniques we have so far. It is noteworthy there are still few reports on the heterostructures with other substrates other than STO.

Nevertheless, there exist reports where extra degrees of freedom are added on the STO layer by the strain effect [74]. Thanks to the good compatibility of STO with many other transition metal oxides, it is possible to apply a wide range of strain on the epitaxial STO film, from tensile to compressive (**Fig. 1.7**). The systematic study by Bark etc [37] showed that the conductivity at the LAO/STO heterointerface persists in compressively strained STO; however, larger thickness threshold of LAO layer is needed for the appearance of conductivity. On the other hand, the conductivity is destroyed in the structures with tensile strain on the STO layer. In addition, it was found that with the increase of the compressive strain, the carrier density at the heterointerface decreases and, thicker LAO layer is required to be conducting. According to the first-principle calculation, these effects are ascribed to the strain-induced polarization in STO, which contributes to overcome the polar field from the LAO films partially. For the strain effect on the transport behavior of the oxide heterostructure, I will discuss more in chapter 4 in the context of tuning the spin-orbit interaction in asymmetric oxide heterostructures.

Figure 1.7 The horizontal line shows the lattice constants of pseudotetragonal or pseudocubic (in angstroms) transition metal oxides commonly used in experiments. It offers a guide for the strain engineer in the synthesis of oxide heterostructure for the properties modification. From Ref. [74]

1.4 Outline of the thesis

In this thesis, I will present the works I have done during my Ph.D. study, which focuses on the two-dimensional transport in oxide heterostructures. The equipments and techniques used in the projects will be briefly introduced in chapter 2. The major works will be introduced in chapter 3 and 4: In chapter 3, I will demonstrate the electric field effect of the LaAlO₃/SrTiO₃ heterostructure using the electric double layer transistor, where the two dimensional insulator-metal transition and electrostatic tuning of the Kondo effect are studied. Chapter 4 is dedicated to the study of the spin-orbit interaction in asymmetric oxide heterostructures. Finally, in chapter 5 I will make a concluding summary for my thesis work and a prospective will be given too.

Chapter 2

Experimental techniques

In this chapter, a brief introduction about the equipments and techniques employed in my thesis works is provided. As a key procedure for the preparation of the oxide heterostructures, the treatment methods of substrates to have pure terminations, i.e. the TiO_2 terminated SrTiO_3 and AlO_2 terminated LaAlO_3 are introduced first. The state-of-the-art pulsed laser deposition (PLD) system with the installment of reflection high energy electron diffraction (RHEED), which facilitates the ability to control the termination of film *in situ*, provides us with the capability to grow the high quality films with atomic-scale control for the following study. Before the transport measurements on the prepared oxide heterostructures, their quality is characterized and confirmed by the atomic force microscopy (AFM), X-ray diffraction (XRD) and transmission electron microscopy (TEM). The brief introduction to these characterization techniques are given in section 2.2. Finally the transport measurement methods and equipments are introduced, which constitute the core measurements in my thesis works.

2.1 Thin film growth

2.1.1 Preparation of substrates with pure termination

As introduced in chapter 1, the termination of STO has the important role in deciding

the transport properties of the LAO/STO heterointerface. And in the following chapter 4, the project based on the asymmetric heterostructure also requires the LAO substrate to have pure AlO_2 termination. The preparation of pure terminated substrates thus plays a fundamental role in the growth of heterostructures. For a perovskite oxide with formula ABO_3 , there are two possible terminating layers in $[001]$ crystallographic direction, i.e. AO and BO_2 . Theoretically the preferential termination should be expected on the surface of a ternary transition metal oxide due to the different surface energy of the two terminations. However, normally the as-received substrates contain a mixture of both termination layers, like STO with the SrO and TiO_2 terminations mixed, and also have several kinds of defects on their surfaces due to the cleaving and polishing processes. Fortunately, the physical and chemical properties of the different terminations make them response differently to the same chemical and/or thermal procedures, which is used to enable the selective etching process on the substrate to obtain high quality pure terminated surfaces.

In my projects, two main substrates, STO and LAO, are used, both of which are required to have single terminated surface, TiO_2 for STO and AlO_2 for LAO. In the following content, I will introduce the process methods used in my experiments, respectively.

a. TiO_2 terminated SrTiO_3

In SrTiO_3 , the SrO component is basic oxide, which tends to react with acid to form salt and water, and TiO_2 is acidic oxide, resistible to react with the acid. Therefore, they have different dissolution rates in the acid environment, which makes it possible

to have selective etch to remove the SrO component on the surface of STO. Since the seminal work by Kawasaki [75], the recipes used for the selective etch have been well developed. For the as-received STOs in our case, they were ultrasonically soaked in deionized (DI) water for 10-15 minutes, which aims to have selective hydroxylation of SrO. Then the substrates with hydroxide complexes on the surface were dipped in the standard, commercially available ammonium fluoride (NH_4F) buffered HF (BHF) solution for around 30 seconds. Next the DI water was used to rinse out the acidic contamination, followed by a cleaning process with methanol and acetone. In the final step, the recrystallization on the etched surface of substrates was facilitated by annealing them in 1000°C for 2 h in the air.

Besides, there are other methods developed for the treatment of STO surface too, like the “Arkansas method” [76], which uses the HCl-HNO_3 (3:1 vol. ratio) (HCLNO) as solution instead of BHF.

b. AlO_2 terminated LaAlO_3

The as-received LaAlO_3 was cleaned by acetone and methanol first; then it was annealed at 1050°C for 10 h in the air. The resulted good termination of the LAO substrate treated by our group can be confirmed by the AFM images. The last thing is about the annealing environment. To avoid the contaminations, which if exists will grow into particles after annealing, normally the flowing oxygen gas is used [77]. In our case, we conduct the annealing process in the open air, as the environment furnace located is clean enough, which is confirmed by the AFM images.

2.1.2 Pulsed laser deposition

The methods for thin film preparation can be largely divided into two classes: chemical vapor deposition (CVD) and physical vapor deposition (PVD), which is distinguished by whether there is any chemical reaction involved in the growth process or not. The CVD methods stand out when large scale films are required (assumed the materials can be grown by CVD). However, when it comes to the multi-elemental materials, more PVD methods are available, such as molecular beam epitaxy (MBE) and pulsed laser deposition (PLD), which can stoichiometrically transfer the material from the target (or sources in controlled way) to substrate and have the capability to precisely control the thickness of film with the help of RHEED. The transition metal oxide with ABO_3 formula is one of such complex compounds, which is normally grown by the PVD methods mentioned above. In my thesis works, I chose the PLD as the growth method.

The main character of the PLD system falls on the energy source, i.e. laser, used to evaporate the target materials. The energy transfer process from the laser to target relies on the photo-electron interaction, whereby the electrons are excited. Consequently the excited electrons transfer the energy to the lattice and lead to the heating process on the surface of the target. This is a transient process, in time scale of picoseconds. As a result, the instantaneous, intense energy vaporizes the materials on the target surface in form of plasma. Furthermore, the energy of the generated plasma will be amplified via absorbing the energy from the remaining laser beam (duration of laser in nanoseconds scale), which is called “laser supported absorption”.

At the same time, the generated plasma expands due to the high pressure gradient from the surface of the target to the surrounding space. Most of the species in the plasma propagate in the direction normal to the target surface, where the substrate is located with certain distance away from the target. The kinetic energy of arriving species is normally in the range of 5-50 eV [78], which is high enough to offer the species high diffusivity on the heated substrate surface and, however, not that high to damage the surface of the substrate. In order to have perfect quality and precise thickness control of the grown thin film by RHEED, the layer-by-layer or step-flow growth modes are required, which can be obtained through adjusting the growth parameters, such as the misfit of substrate, growth temperature, pressure, laser energy, etc.

Figure 2.1 Schematic structure of pulsed laser deposition (PLD)

Figure 2.1 shows the schematic structure of PLD system used in our group. The main system was designed by the Twente Solid State Technology (TSST), Netherland, along which the Coherent Compex Pro 102F laser system is used, with 248 nm wavelength and 20 ns duration. In this set-up, the laser is introduced, guarded by mirrors, and focused on the target surface by the lens outside of the window, shown in the schematic in **Fig. 2.1**, through whose position the spot size of the laser can be adjusted. Another central component of the system is the heating stage, which functions as holder of substrates during the heating process. In this setup two heating methods are provided: resistive heating and laser heating, which are designed to have a large temperature range (from room temperature to over 1100 degree by design) to enable the growth of versatile materials. In both types of heaters, substrate is loaded/unloaded in every deposition. In the front of heating stage with certain distance, there is target holding component, which can move in horizontal and/or vertical direction during the film growth by remote control so that the ablated area on the target can vary without changing the relative position between the substrate and plume. The target holding component is designed to be able to hold 5 targets at the same time, which thus guarantee the ability of the synthesis of multilayer structures. To keep the vacuum inside the chamber as clean as possible, the loading and unloading of the heater and target are performed via the loadlock chamber. In addition, the installed RHEED can be operated to *in situ* monitor and diagnose the growth of thin film even at high environment pressure, thanks to the developed differential pressure system in this setup.

Below I will brief introduce the operation principles for the growth of films used in my projects, but the detail parameters for the oxide films studied in my thesis works will be presented in the chapter 3 and 4.

First, the substrate is fixed on the heater using silver paste, where special cares are paid to make sure that the substrate is fixed evenly to guarantee the homogeneously heating of the substrate in the following process. For the STO substrate, to which the oxygen vacancies are easily introduced in high vacuum environment, it is heated to 800 °C in the oxygen rich environment (0.4 mbar); while for the LAO substrate, it is normally heated at the same pressure as the one used when the film is grown. When the desired temperature is reached, in general we wait half an hour before starting the deposition, during which the background pressure for growth is set and the RHEED system is turned on and adjusted to the proper parameters for monitoring the film growth. The films of STO and LAO can grow in the layer-by-layer mode in proper growth parameters, which enables us to *in situ* monitor the thickness of the growing film and get desired thickness of the growing film. After growth, the film is cooled down to room temperature at certain rate. For LAO/STO heterostructures, in order to suppress the influence of possible oxygen vacancies introduced during growth, the oxygen gas is introduced, with around 400 mbar background-pressures, after the growth finishes, and an annealing step at 600 °C for about 1 hour is adopted before the film is further cooled down to the room temperature.

2.1.3 Reflection high energy electron diffraction (RHEED)

The ability of *in situ* monitoring and diagnosing during the growth of film is one of the main features of the PLD system I used. It offers us the power to precisely control the thickness and hence also makes the control of termination of the ultrathin film possible. From the aspect of adjusting the growth parameters for a new growth, it also offers helpful guides.

RHEED is a surface sensitive (down to monolayer) characterization method based on the forwarded reflection of the incident electrons being with high kinetic energy and low impact angle. As shown in **Fig. 2.2a**, the RHEED system contains three components: electron source, phosphor screen and clean sample surface. The incident electrons act like waves due to their high kinetic energy. After elastically scattered by the atoms on the surface of substrate or film, the diffracted electrons constructively interfere at certain angle in accordance with the lattice structure on the surface of substrate or film and the wavelength of the incident electrons. The resulted distribution of electrons waves, i.e. the diffraction pattern, is manifested on the phosphor screen after the electrons collide with it. It is this diffraction pattern that offers us the information about the real-time crystallography of the sample surface. Initially the RHEED system can only be operated in rather high vacuum condition ($< 10^{-5}$ mbar) to ensure the incident electrons with high enough kinetic energy before reaching the surface of the substrate or film. Because of the development of the differential pressure system, now it can also work in high background growth pressure, up to 1 mbar for the commercial PLD systems.

The intensity of the diffracted pattern depends on the roughness of the surface, which is the foundation for its application for *in situ* monitoring of the thickness of the growing film. As the surface coverage, corresponding to the roughness of the surface, changes during the film growth, the intensity of the pattern will change accordingly, resulting in a periodic oscillation with time (red curve in **Fig. 2.2b**). It is this feature that enables us to *in situ* monitor the thickness of the growing film. The **Fig. 2.2b** shows the typical phases in a single period corresponding to a monolayer growth of a film.

Figure 2.2 (a) Schematic diagram of the setup of the reflection high energy electron

diffraction (RHEED). (b) Time dependence of the RHEED pattern intensity, where the cartoons represent the surface conditions (coverage) at different phases of a single period of the intensity.

2.2 Structural characterization

After the growth of the films, the quality of them and their interfaces is characterized by the X-ray diffraction (XRD) and transmission electron microscopy (TEM). In addition, the flat surface of the grown films is further confirmed by the atomic force microscopy (AFM), which is also employed to verify the quality of single-terminated surface of the treated substrates.

2.2.1 X-ray diffraction (XRD)

The comparable length scale of the wavelength of x-ray to the spaces of lattice structure makes the XRD be one of the powerful methods to characterize the crystal structure. The diffracted electrons waves with certain wavelengths by a specular solid plane interfere constructively at certain angle, depending on the lattice structure of the solid, which follows the same principle as that of the RHEED. In other words, the resulted diffracted patterns offer the information of the solid structure, which is the base for the well-developed science of crystallography. The classical model to understand this is the Bragg's law, $2d_{hkl}\sin\theta = n\lambda$, as schematized in **Fig. 2.3**, which gives the angles of the coherent reflected electrons waves and in turn offers the simple principle to calculate the lattice constant from experiment measurements

Figure 2.3 Schematic description of the Bragg's law

The XRD measurement for the epitaxial films offers valuable information, such as the crystal quality (poly- or single crystals), crystal orientation, lattice constants, layer information (thickness, density and roughness), etc. However the particular information requires certain kind of measurement methods. The following three analyses methods are the ones in common use in the characterization of epitaxial films.

- **Theta-2theta scan** is a coupled scan, which was used to confirm the orientation of an epitaxial film and get the lattice constants.
- **X-ray reflectivity (XRR)** is used to determine the thickness, density and roughness of an epitaxial film (or each layer in a multilayer structure). It works relying on the interference of multiple reflected waves from surface and interfaces between layers. Such a technique requires the incident x-ray with small angle, normally in the range from 0 to 10 degree.

- **Reciprocal space mapping (RSM)** can offer rich information about the films.

The observed position and shape of the reciprocal lattice points with respect to that of substrate can reveal the information about the mismatch, relaxation, strain state, dislocation density, mosaic spread, etc.

2.2.2 Transmission electron microscopy (TEM)

When the size of materials is down to nanometer scale, or even the atomic scale (interface in our oxide heterostructure cases), the visible light can no more have the ability to magnify them above the resolution of human eyes due to the limit imposed by the wavelength of the visible light. It is in this length scale that the TEM technique takes the leading role because of the extremely small de Broglie wavelength of the high-energy electrons, and the resolution of TEM can reach to the order of a few angstroms (10^{-10} m). Analogue to the light microscopy, the magnification of a object is obtained with the help of electromagnetic lenses, instead of glass lenses in light microscopy. Besides the direct image observation, other valuable information can also be obtained, such as selected area diffraction, electron energy loss spectroscopy, etc.

The properties of oxide heterostructures strongly depend on their structural, chemical quality, like structure defects, composition, interface sharpness, dislocation, and even the oxygen vacancies distribution, etc. All these can be properly characterized using the TEM. In the LAO/STO heterostructure, as introduced in chapter 1, the interface plays an important role on the observed exotic properties. In

some reports, the interdiffusion of cations is claimed by some groups to contribute to the conductivity [68]. Therefore the TEM has been used to demonstrate the sharp interface of the LAO/STO heterostructures grown in our group, as shown in **Fig. 2.4**, to exclude the influence of the cations interdiffusion on the performance of the resistive switching devices based on the LAO/STO heterostructure [79].

Figure 2.4 Cross-sectional TEM image around the interface region for LAO/STO heterostructure.

2.2.3 Atomic force microscopy (AFM)

AFM is a lab tool widely used for surface imaging with nanometer-scale lateral resolution and sub-nanometer-scale vertical resolution. Unlike the scanning tunneling microscopy (STM), which relies on the current tunneling process between the sample surface and the tip, the AFM technique can be used to scan any sample

surfaces, conducting or insulating, as it “sees” the sample surface through the molecular force between the tip and sample surface. As shown in **Fig. 2.5**, the system consists of cantilever with sharp tip at the end, light-lever system and piezoelectric scanner. When the tip is in proximity to the sample surface, the molecular force between the tip and sample will deflect the cantilever, which is recorded by sensitive photodiode via the reflected laser beam off the surface of the cantilever. After a raster scanning process, precisely controlled by the piezoelectric scanner, the topographical image of the scanning area can be obtained.

Figure 2.5 Schematic diagram for the operational principle of AFM

The sub-nanometer-scale vertical resolution makes the AFM a good way to characterize the terrace surface of the treated substrates. And it also offers valuable information which can help to optimize the growth parameters of the high quality thin films.

2.3 Transport measurements

The transport measurements are the main content of my thesis, which offers the tool to reveal the physical insights behind the physical phenomena of conducting oxide heterointerface. Most of the physical properties discussed in this thesis are resulted from the transport measurements. In general, the transport parameter, i.e. resistivity, of the samples is studied as function of temperature, electric and magnetic field, from which the carrier density and mobility can be calculated. Furthermore, the exotic physical phenomena, such as insulator-metal transition, Kondo effect and electron localization, are able to be inferred and novel device concepts can be explored.

2.3.1 Measurement configurations

The transport measurements in most parts of my works were performed with four-terminal configuration, so as to avoid the influence of the contact resistances, which is an unavoidable problem in transport measurements on the oxide heterointerfaces. The Hall bar and van der Pauw geometries are the typical four-terminal configurations, both of which were used in my thesis works.

- **Hall bar method.** Figure 2.6a shows one of the typical geometries of the Hall bar. Besides the normal resistance measurements, it is used to perform the Hall effect measurement, as shown in figure, with extra magnetic field applied in out-of-plane direction, from which the carrier density and mobility of the channel are calculated.

Figure 2.6 Hall bar (a) and van der Pauw (b) geometries for the four-terminal transport measurement.

- Van der Pauw method.** Van der Pauw is an alternative and more flexible method to conduct the normal resistance and Hall Effect measurements, whose typical configuration is shown in **Fig. 2.6b**. In this method, the resistance $R_{12,34}$ is obtained via measuring the voltage between contacts 3 and 4 while the current is entering through contact 1 and leaving via contact 2. Before getting the final resistance of a sample, the resistances with different current-flowing channel (thus with different contacts for voltage measurement), such as $R_{23,41}$, $R_{34,12}$, $R_{41,23}$, are required to be measured. However, using the van der Pauw technique requires careful attentions to the following issues: the electrodes should be at the

circumference of the sample and as small in size as possible; the film in study should be uniform.

2.3.2 Measurement equipments

- **Physical properties measurement system (PPMS, Quantum design)**

The PPMS system offers a powerful platform for versatile transport measurements. The PPMS system used in my experiments, as shown in **Fig. 2.7**, is equipped with Ever-Cool system with the temperature range of 2-400 K, which can even go down to 0.35 K with the help of Helium-3 refrigerator. The magnetic field can reach up to 14 T with a superconducting coil. Furthermore, the open architecture of it makes the third-party instruments available to the PPMS hardware, because of which we can apply the gate voltage to the field effect devices. And this can also extend the measurement range of conductivity of the sample, which is necessary for the measurements on the samples with high resistances.

Figure 2.7 Image of PPMS system in PAP division.

- Besides the PPMS system, I also adopted the Keithley 4200-SCS Parameter Analyzer and Janis Closed Cycle Refrigerator System with home-built measurement system to conduct comprehensive transport study on some of the samples studied in my works.

Chapter 3

Electric field effect of the $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures^{*}

3.1 Introduction

The correlated charge, spin, orbital, and lattice degrees of freedom in transition metal oxides make them an attractive platform to explore rich physics and potential applications [2,80]. Oxide interfaces offer even more exciting opportunities due to the emerging effects such as broken inversion symmetry, exchange interaction, and spatial confinement [12,81], which is well exemplified by the LAO/STO heterostructure, as discussed in chapter 1. One defining feature of the interface conduction is the thickness dependence, i.e., it is insulating when the LAO thickness is below four unit cells (uc), whereas the conduction emerges above the critical thickness [36]. Furthermore, the carriers in the two-dimensional electron gas (2DEG) are confined within several nanometers near the interface as a result of broken symmetry, and the profile of distribution has a sensitive dependence on the carrier density [64,66,82-84]. Based on the 2DEG at the LAO/STO interface, nanoscale control of the insulator-to-metal transition using local probes has also been demonstrated [85-86].

^{*} Most parts of this chapter are from the published paper: *Adv. Mater. Interfaces* **1**, 1300001 (2014)

It is noteworthy that the recent revelation of magnetism at the LAO/STO interface added another facet to the fascinating physics [4-6,87-88]. Two notable sources were proposed for leading to the weak magnetism discovered in the LAO/STO heterostructures: One is the intrinsic electron reconstruction [4,89] and the other is the extrinsic oxygen vacancies [90]. In addition, the inhomogeneous distribution of magnetic dipoles as demonstrated in a recent scanning superconducting quantum interference device (SQUID) microscopy study clearly underscores the critical role of disorder in forging the magnetic landscape [5]. In spite of the efforts [4-6,91], the nature of magnetism discovered in samples prepared in a wide range of conditions remains as an issue of debate.

To shed light on the physics of LAO/STO interface and to modulate its properties, electric field effect was proven to be a powerful tool [19,36,44,92-93]. In particular, an insulator-to-metal transition has been achieved by using electric field gating at room temperature [36]. In these previous efforts, the STO substrates were used as the dielectric insulator in the back-gate configuration, and high voltages of tens to hundreds of volts were required. Recently, ferroelectric $\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ was used to bias the LAO/STO interface in a top-gate configuration, and nonvolatile modulation of the 2DEG was demonstrated [94]. As a breakthrough in such electric field effect studies, electric double-layer transistors (EDLTs) with the top-gate configuration were employed to trigger the transformation of ground states in some key materials [95-97]. But, so far there has been no report on applying this powerful technique to exploring the transport properties of oxide interfaces.

In this project we carried out electric field effect experiments on the LAO/STO heterointerface using the EDLT structure. We found that the insulating three uc LAO/STO heterointerface can be electrostatically tuned through an insulator-metal transition, and the transition exhibits a percolative nature. Around the transition, giant linear positive MR was observed due to the present of significant inhomogeneity in transport. At higher gate voltages and above a critical carrier concentration of $\sim 1.69 \times 10^{13} \text{ cm}^{-2}$, Kondo effect manifests in the metallic transport regime, revealing the pronounced role of the magnetic degree of freedom at low temperatures. Overall, our experiments on the electrostatic modulation of LAO/STO interface underscore the importance of electronic/orbital reconstructions and magnetic centers in dictating the general electronic and magnetic properties of oxide heterointerfaces.

3.2 Devices fabrication and operation principle of electric double-layer transistor (EDLT)

3.2.1 Devices fabrication

The 3-uc LAO films were deposited on TiO_2 terminated STO substrates at 800 °C under an oxygen pressure of $\sim 1 \times 10^{-4}$ mbar. During the pulsed laser deposition (PLD), the laser influence was fixed at $\sim 1.5 \text{ J/cm}^2$. The film growth was monitored by *in situ* high-pressure reflection high-energy electron diffraction (RHEED). The RHEED intensity oscillation is shown in **Fig. 3.1a**. In order to minimize the influence of oxygen vacancies, the STO substrates were heated to the designated temperature at an oxygen pressure of 0.4 mbar before the PLD growth, while after growth the

samples were annealed at 600 °C at 400 mbar for 1 h and then cooled down to room temperature at the same oxygen pressure. Before going to next step for device preparation, the quality of the samples were confirmed by the AFM. As shown in **Fig. 3.1b**, the topography with the smooth terrace demonstrates the high quality of films.

Figure 3.1 Device preparation and characterization. (a) RHEED intensity oscillation as a function of deposition time, showing the layer-by-layer growth mode for the pulsed laser deposition (PLD) synthesis of 3 uc LaAlO_3 (LAO) on a TiO_2 -terminated SrTiO_3 (STO) substrate. (b) Atomic force microscopy topography for the 3 uc LAO on TiO_2 -terminated STO. (c) Optical micrograph of a device after the electrode (Ti/Au) deposition. (d) Typical I - V curve tested on the prepared device at room temperature which shows the ohmic contact of the electrodes. In this particular device, the room-temperature sheet resistance is about 3.3 $\text{G}\Omega$.

Subsequently, the Ti/Au contacts with pattern were deposited by electron beam evaporator and/or thermal evaporator. First the standard photolithography technique was used to expose the areas where the electrodes would be deposited. Because of the low work function and good contact with the films, the Ti was selected as the electrode material in our devices. In order to avoid the oxidization of the Ti films once exposed to the air and ionic liquid, an Au capping layer was deposited whose pattern is shown in **Fig. 3.1c**. The thicknesses of the Ti and Au metal films are 30 and 70 nm, respectively. Next the diamond knife with very fine tip was utilized to isolate the channel and electrodes for transport study from the remnant part of the film. Actually we were able to make use of the standard photolithography technique to selectively grow the film with hall bar pattern too. However, in order to avoid the possible contaminations introduced into the interface during this process, we chose the former method (named as “selective isolation method”) to get the hall bar, whose performance was confirmed by the transport measurements introduced later. The I-V scan was performed to check the quality of the contacts after making the electrodes. As shown in **Fig. 3.1d**, the ohmic contact guaranteed the more reliable and sustainable performance during the measurements. After this, the Au wires were attached to the electrodes of the device before it was fixed at the holding puck for transport measurements. Finally the silicone was used to confine the area, including the channel area, where the ionic liquid was dropped to avoid contact with the connections between the wires and electrodes and therefore damage of the connections. However, on the other hand, the confine area should be reasonable large to involve as large gate electrodes area as possible to obtain high modulation capability.

3.2.2 Operation principle of electric double-layer transistor

The electrostatic doping in novel materials offers opportunities to result in modification of electronic and magnetic properties in a controllable and reversible way [98]. The resulted carrier density dependent phase diagram provides invaluable information for understanding the physics insight behind the novel materials or systems. Even so, the working principle of it is simple. **Figure 3.2a** shows the schematic of a typical conventional field effect transistor. In semiconductor devices, the channel and the regions under the source/drain electrodes are purposely doped into the ones with different types of majority carriers, like the channel is p-type doped while the source/drain regions are n-type doped. When no gate biases are applied, the forming p-n junction pairs between channel and source/drain regions will not allow current flow through the channel, which is the “OFF” state. The “ON” state is turned on only when a large enough gate bias is applied. In this state, the applied electric field penetrates into the semiconductor and attracts the minority carriers to accumulate at the interface between the dielectric and the underneath semiconductor, therefore forming the channel with the same type carrier with the source/drain regions and thus removing the depletion zones between the channel and source/drains regions to allow the current flow under a source/drain bias. With a fixed source/drain bias, the strength of the current flow can be tuned by modulating the carrier density in the channel by the electrostatic field. It is this simple principle that is borrowed in the studies of the novel materials and systems using field effect transistors.

In the transistor based on the novel materials, like transition metal oxides discussed in this thesis, the initial state of the channel depends on the materials itself, which

can be insulating, conductive or very conductive, etc. In such devices, the quantitatively control of the electronic and/or magnetic properties, or the different phases under various carrier density ranges, rather than the “ON”/ “OFF” states, are needed. Normally, the wider range the carrier density can be tuned, the more information one can gain. However, this tuning capability is limited by not only the dielectric constant of the solid dielectric but also the geometric structure of the transistor, where the thickness of the solid dielectric cannot be too thin due to the concern of leakage current through it. Such a scenario can be understood by a simple capacitor model, whereby the gate electrode-solid dielectric-conducting channel can be ideally seen as a parallel-plates capacitor, whose capacitance is

$$C = \frac{\epsilon_0 \epsilon_r A}{d} \quad (3.1)$$

where the ϵ_0 and ϵ_r are the vacuum permittivity and dielectric constant, A is the area of the gate electrode, and d is the thickness of the solid dielectric. It is known that to store more charges in such an ideal capacitor under a fixed bias requires larger capacitance. According to the equation (3.1), the larger capacitance can be achieved by using dielectric with larger dielectric constant, enlarging gating area, or reducing the distance between accumulation layers. In other words, these factors are also the ones that make the limit on the capacitor (and thus on the conventional transistors). Normally, the carrier density range tuned by the conventional field effect transistor can reach $\sim 10^{13} \text{ cm}^{-2}$ and in certain cases, it is technically possible to reach around $(1-3) \times 10^{14} \text{ cm}^{-2}$ by using ferroelectric dielectric or other efforts [98]. Nevertheless, since for many strong correlated materials, the interesting physical properties are presented on the verge of the capability of the conventional transistors, it is kind of challenge to have the comprehensive study on them using the conventional transistors.

The recent developed electric double-layer transistor (EDLT) offers alternative structure to fulfill the electrostatic doping with more powerful capability, which can induce carrier density to the range of $10^{14} \sim 10^{15} \text{ cm}^{-2}$ and has successfully extended the application of the electrostatic method to many novel materials and helped to observe many insightful phenomena, such as the quantum transition between the superconducting and insulating state [96-97], abnormal Hall effect [99], etc. **Figure 3.2b** shows the schematic of the EDLT, from which we can see that the configuration is the same as the conventional counterpart except that the ionic liquid is used as the dielectric instead of the solid one. The operation principle is also same, i.e. tuning the carrier density by the gate bias through the electric field delivered by the dielectric. The main difference comes from the micro-mechanism that the electric field is delivered from the gate electrode to the channel, as explained below, which endows EDLT the superior tuning capability.

Figure 3.2 Schematics of the conventional field effect transistor (a) and novel electric double-layer transistor (EDLT) (b). Figure (c) and (d) show the potential

change (green curves) across the solid dielectric and ionic liquid in these two kinds of transistors. The EDL is referred as electric double layer. Note that the space for EDL here is exaggerated here for clarification and the schematics here are in the cases with positive gate bias.

Ionic liquids are salts comprising the organic cations, and organic or inorganic anions, thus possessing comparative ionic conductivity. In the EDLT structure, the source/drain electrodes, gate electrode and surface of channel are in contact with the liquid. When the positive gate bias, for example, is applied, the cations (anions) will move toward the channel surface (gate electrode) and accumulate there, thus forming the electric double layer (EDL) in both liquid-solid interfaces when equilibrium under the bias reaches, shown in **Fig. 3.2b**. As a result, in contrast to the conventional transistors, where the potential changes continuously across the solid dielectric, the potential drop occurs only in the EDLs at both interfaces, which can be seen as parallel-plate capacitors too. The schematics of the potential drops for these two types of transistors are shown in **Fig.3.2c** and **d**, respectively. Because the space in EDL is typically in length of *nanometers* (even angstroms depending on the size of the ions), the potential drop in such small space can lead to a huge local electric field and thus can effectively modulate the carrier density of a larger range in the underneath channel, which can also be understood by the simple capacitor model. The feature of potential drop only at EDLs also eases the preparation of the device, which allows to have a flexible position of gate electrode, not like that in conventional counterparts, where gate electrode should be as close to the channel as possible before the obvious leakage happens. Therefore, we chose the EDLT as the technique to perform the study of the electric field effect of the LAO/STO heterostructure.

Figure 3.3 Schematic of the EDLT on the LAO/STO heterostructure (a) and the cross-section of the channel in case with the positive gate bias (b).

In our devices, the ionic liquid N, N-diethyl-N-(2-methoxyethyl)-N-methylammonium bis (trifluoromethylsulfonyl) imide (DEME-TFSI) was chosen as the gate dielectric material because of its capability of generating strong electric field upon bias voltage [95,97]. The schematic structure is shown in **Fig.3.3a** and the cross-section of channel under the positive gate bias is also illuminated in **Fig. 3.3b**. It is totally frozen below 180 K, which results in negligible leakage current and facilitates accurate transport measurements at lower temperatures. Initially, the device channel was insulating as expected for the three u.c. LAO/STO heterostructure, and the resistance is beyond our measurement limitation of $10^9 \Omega/\square$. As a general protocol, gate voltages were applied for 30 minutes at 210 K which is above the frozen point of the ionic liquid. Subsequently, the devices were cooled down to 180 K, below which the transport measurements were performed. Before applying another gate bias, the device was heated up to 210 K to erase the charges

accumulated in the previous run. The Keithley 2635A source meter was employed to apply the gate voltages, and the transport data were collected using the physical properties measurement system (PPMS, Quantum Design). Upon increasing positive gate voltage, the conduction of the interface was progressively enhanced. We note that the devices returned to their insulating pristine state when the gate voltage was removed, which ensures that there is negligible chemical reaction between the ionic liquid and the LAO layer under the measured conditions [100]. In this chapter, I will present data collected on three typical devices with the identical structure and in the following sections I refer to them as LS-1, LS-2 and LS-3, respectively. Here, it should be noted that I also fabricated EDLT devices with the LAO layers being 6 and 10 u.c., but the tuning effect was not as significant as the 3 u.c. case.

3.3 Two-dimensional insulator-metal transition at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface

3.3.1 The insulator-metal transition

The band theory gives the general definitions of metal and insulator based on the non-interacting or weakly interacting electron systems, whereby the highest filled band of a metal is partially filled, while it is full-filled for an insulator. And when the gap between the full-filled band of the insulator and nearest empty band is relatively small so that certain amount of electrons can be thermally excited to the empty band easily at finite temperature, it is where a semiconductor locates. The band structure of this elegant theory is simple due to the periodic lattice structure of atoms in

perfect crystal. However, in practical conditions there are other factors, such as electron-electron interaction and disorders in the lattice structure, which are beyond the consideration of the band theory and strong enough to result in total different physical properties from the ones expected by the band theory in certain kinds of solids, like many of the transition metal oxides discussed in chapter 1. The strong electron-electron interaction for the solid with the highest filled band half-filled can split the band into the completely filled and empty sub-bands (i.e. the lower and higher Hubbard bands) and therefore result in the insulating state which is supposed to be metallic according to the band theory [80]. The resulted insulator is called Mott insulator, which is the “parent” compounds of the high temperature superconductors. On the other hand, the metallic state can also be modified into insulators by strong-enough disorders in the lattice structure, generating the so-called Anderson insulators [101]. In addition to these, the strong electron-lattice interaction and the charge/spin density wave (CDW/SDW) in low dimension materials are also able to localize electrons.

These efforts to understand why the certain solids are insulators, especially the ones beyond band insulators, in turn stimulate the study on how one can control the transition from the insulating state to the metallic state. In the bulk systems, this is normally achieved by the doping process, the typical cases of which are the high temperature superconductors and colossal magnetoresistance manganites. However more exotic phenomena turn out in 1D and 2D systems due to the dimensional confinement. For 1D matter, it is accepted that there are no metallic states at zero

temperature, and there is insulator-metal transition due to the thermal excitation at certain finite temperature, which is well described by the Luttinger liquid theory. In the case of 2D system, the insulator-metal transition driven by the carrier density doping is still an on-going debating issue [102-104], which is normally discussed in Si MOSFETs [103] and GaAs/AlGaAs heterostructures [104]. The transition is normally indicated by the observation of the qualitative change of the temperature dependence of the resistivity induced by change of the carrier density. Hence there is a critical carrier density n_c , which separates the insulating state ($n < n_c$), exhibiting $d\rho/dT < 0$ from the metallic state with $d\rho/dT > 0$ at a finite temperature range experimentally. The controversial issue comes from whether or not the metallic behavior can persist all the way down to zero temperature. In the Fermi liquid theory, there is no finite conductance for a infinite large 2D system at zero temperature and thus the observed metallic behavior just exists at a finite temperature range, whose conductance will disappear at zero temperature due to the quantum conduction correction according to the one-parameter scaling theory of localization [101]. Therefore the two-dimensional insulator metal transition is regarded as a classical-quantum crossover transition. As a result, this carrier density induced transition can be modeled by the conventional two-dimensional percolation theory, which in turn becomes a critical criterion for the scenario [104-105]. Alternatively, the other scenario proposes that the observed metallic behavior is a real one, being able to persist down to zero temperature and regards the transition as a quantum phase transition [102,106]. Here as the insulator-metal transition tuned by the EDLT

on the LAO/STO heterostructure is consistent with the features of the classical-quantum crossover transition, I will focus on the introduction of the two-dimensional percolation transition below. The quantum phase transition is beyond the scope of my thesis, and readers can be referred to many reviewed papers[102,106].

The percolation transition scenario in 2D systems implies the existence of the inhomogeneous potential landscape around the transition, which is ascribed to the charged impurity scatterings and their random distribution [103-105,107-108]. In the metallic regime with high carrier density ($n > n_c$), the carriers screen completely the disorder potential and thus no inhomogeneous potential is observed. Then as the carrier density decrease to low enough range, the disorder potential cannot be totally screened anymore. The resulted inhomogeneous potential landscape consequently gives rise to the inhomogeneous distribution of the carrier density with the appearance of the insulating depletion zones and the conducting accumulation ones. As a result, the conductance decreases with a strong dependence on the carrier density. Eventually once the carrier density reaches the threshold ($n < n_c$) with the depletion regions blocking the percolation conducting path across the whole 2D system, the insulator emerges. Such a transition process can be well modeled based on the relationship between the carrier density and the conductance [104-105]

$$\sigma = K(n - n_c)^\delta \quad (3.2)$$

where δ is the critical exponent related to the dimensionality of the studied system, which is $4/3$ for an ideal 2D system, n_c is the critical percolation density and K is a constant of proportionality.

3.3.2 Experimental results

In **Fig. 3.4** the temperature-dependent sheet resistances at various gate voltages are plotted for the device LS-1. In the low voltage regime, i.e., $V_g < 0.4$ V, the interface remains insulating. At gate voltages between 0.4 and 0.7 V, a transition to metallic transport was observed around the quantum resistance $h/e^2 \sim 25.8$ k Ω , indicating that the accumulated electrons form a two-dimensional system. This threshold voltage of 0.7 V for the onset of metallic channel transport is consistent with the polar catastrophe model which was often cited to explain the dependence of the LAO/STO interface transport on the thickness of LAO layer [61]. In this model, charge transfer occurs between the valence band of LAO and the conduction band of STO when the tilting of the LAO band is more than the band gap of STO, i.e., 3.2 eV. If we assume that the built-in field in each LAO layer is roughly the same, then the critical thickness of 4 uc LAO corresponds to a built-in field of 0.8 V/uc, which is close to the value of 0.24 V/Å calculated using first-principles methods [62]. Thus, the formation of electric double layer induced by a gate voltage of 0.7 V is equivalent to adding one uc of LAO in triggering the metallic transport in the LAO/STO channel. When the gate voltage is above 0.7 V, a stronger electric field is exerted on the heterointerface and thus it is expected that more carrier would be introduced to the interface channel. As a result, we observed a set of remarkable

temperature-dependent transport behaviors, which are the focus of this work. In general, as the temperature goes down from 180 K, the resistance first decreases, i.e. $dR/dT > 0$, which can be ascribed to the suppression of electron-phonon scattering, thus indicating that the metallic behavior in the LAO/STO heterointerface has been achieved by the gate bias. Then, a resistance upturn emerges at a certain critical temperature ($T_{\min}$), leading to a minimum resistance. This transition between two opposite temperature-dependent behaviors clearly indicates that different competing mechanisms are involved in the transport. Furthermore, compared to the high-temperature regime, the resistance upturn responds more strongly to the electrostatic gating. The similar tuning behavior was observed in the other devices too, as shown in inset of **Fig. 3.4** for the device LS-2.

Figure 3.4 Temperature-dependent sheet resistance of the LAO/STO interface as a function of gate voltage (V_g) measured on the sample LS-1. For the sake of clarity,

the 0.4 V data was normalized by a factor of 1/10. Inset shows the same tuning effect on LS-2.

Figure 3.5 (a) Temperature of the minimum sheet resistance ($T_{\min}$) as a function of V_g . (b) Logarithmic plot of the gate-dependent sheet carrier density obtained at 180 K.

More importantly, we found that the $T_{\min}$ does not vary monotonically upon the increase of gate voltage, as shown in **Fig. 3.5a**. We also found that the low-temperature resistance upturn and the non-monoclinic gate modulation of $T_{\min}$ are general behavior, which were observed in the other devices we prepared. We divide the gate-dependent transport into two regimes separated by a critical gate voltage $V_C \sim 1.7$ V. In previous reports, the resistance upturn in LAO/STO heterointerfaces was attributed to the weak localization as a result of the interface disorders [42,44], and the Kondo effect which hints a magnetic origin [4]. However, the different synthesis conditions in the literature works presumably led to different transport characteristics of the 2DEG, and so far the exact mechanism of the

resistance upturn remains ambiguous. One advantage of our experiments is the continuous electrostatic modulation of the carrier density over a large range, which enables us to distinguish the various scenarios behind the interfacial transport behavior.

To shed light on the electrostatic tuning, the density and mobility of the carriers in the channel were obtained using the Hall-effect measurements. The measured sheet carrier density (n_s) at 180 K as a function of gate voltage is plotted in **Fig. 3.5b**. Notably, n_s changes quasi-linearly over the whole range of gate voltage. The effective capacitance C_g is estimated from the relationship $C_g/e = dn_s/dV_g$ to be around $2.5 \mu\text{Fcm}^{-2}$. This value is smaller than the capacitance of EDL reported for the ionic liquid [109], which can be ascribed to the fact that the channel in our device is the LAO/STO interface instead of a bare oxide surface. We found that the critical gate voltage of 1.7 V corresponds to a carrier density of $\sim 1.69 \times 10^{13} \text{ cm}^{-2}$, which is close to the critical density at the universal Lifshitz transition between different d orbitals as reported by Joshua et al [110]. Data here were obtained from LS-1.

Figure 3.6 Hall Effect measurements at gate voltage (a) $V_g = 1.1 \text{ V}$ and (b) $V_g = 3.0 \text{ V}$

V, where the bold grey line is for experimental data and the red curve for the fitting.

Data here were obtained from the measurement on LS-2.

Figure 3.7 Carrier density and mobility tuned by gate voltages. Temperature dependence of (a) sheet carrier density n_s and (b) mobility μ measured at various gate voltages. Data here were obtained from the measurement on LS-2. Inset of fig. b shows its temperature of the minimum sheet resistance ($T_{\min}$) as a function of V_g .

To further explore the transport properties in the LAO/STO heterointerface by field effect, we also measured the temperature dependent carrier density and mobility. **Figure 3.6** shows the typical Hall effect measurements for device LS-2 at field range between -4 and 4 T at low and high gate regime. The resulted temperature dependence of carrier density and mobility is shown in **Fig. 3.7**. The nearly temperature-independent carrier density at the various values of V_g indicates that the interface is in the metallic regime. Considering also the transport data in **Fig. 3.4**, we can conclude that a conducting 2DEG is achieved at the LAO/STO heterointerface through electrostatic gating in the top-gate device configuration. As

shown in **Fig. 3.7b**, at $V_g = 0.9$ and 1.1 V, which is smaller than the critical gate voltage V_C , inferred from the inset, the mobility μ decreases at temperatures below 10 K. On the other hand, at $V_g = 2.8$ and 3.0 V, which is larger than the critical gate voltage V_C , n_s reaches $\sim 2\text{--}3 \times 10^{13} \text{ cm}^{-2}$ and $\mu \sim 1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 2 K. These high- V_g results are consistent with the reports on the conducting LAO/STO interfaces [36,91,93]. The negligible modulation of the high-temperature values of μ by the gate voltages indicates that the field effect in the range of $T > T_{\min}$ relies on the tuning of carrier concentration n_s . On the other hand, the effect on the low-temperature ($< T_{\min}$) resistance upturn is dominated by the modulation of mobility, which indicates that the scattering mechanisms in the carrier transport in our heterostructures evolve with the gate voltages.

When the gate voltage and the carrier density are low, the 2D transport of heterointerfaces may present an inhomogeneous character since the distribution of itinerant carriers is not perfectly uniform. To shed light on the nature of the gate-induced insulator-to-metal transition, we plot the sheet conductance versus the carrier density obtained at 10 K in **Fig. 3.8**. Notably, the evolution of the conductance with the carrier density follows the percolation transition model, i.e. equation (3.2). Our fitting yields $\delta \approx 1.3$ and $n_c \approx 4.5 \times 10^{12} \text{ cm}^{-2}$. The value of δ corroborates with the general critical exponent of 2D percolation transitions of $4/3$. This implies that the 2D character of the conducting interface is retained during the electrostatic doping. We also note here that the derived n_c is quite low, and even at higher electron densities the effective metallic phase exhibits an insulator-like sign

of $d\sigma/dT$ (>0) down to very low temperatures, which is similar to the previous results obtained in n -GaAs heterostructures [104]. It is noteworthy that disorders and random potentials play an important role in dictating the transport of our devices, and the downturn of mobility observed at low temperatures and gate voltages (**Fig. 3.7b**) clearly implies the existence of significant scattering in the electron system [111].

Figure 3.8 Double-logarithmic plot of conductance as a function of carrier density measured on the sample LS-1 at 10 K. The gray line is the fitting curve according to the percolation transition model. Inset shows the plot of the conductance vs. the reduced carrier density ($n_s - n_c$), where n_c is the critical density for the percolation transition.

More characters of the percolation transition were provided by the magnetoresistance (MR) measurements. **Figure 3.9a** shows the MR measured at 5 K and various gate voltages, and the magnetic field was applied perpendicular to the interface ($B_{\perp}$). Positive MR with the expected quadratic field dependence was observed at higher gate voltages, which can be attributed to the Lorentz force. On the other hand, anomalous linear MR with colossal magnitudes emerges in the range of low gate voltages, which can be ascribed to the inhomogeneities around the percolation transition. In the classical inhomogeneous model [112-113], the distortion of current path due to the spatial fluctuation of carrier concentration and mobility in the presence of a magnetic field can lead to anomalous linear MR. As shown in **Fig. 3.9b**, the quadratic field dependence still dominates the MR at low magnetic fields, followed by the transition to the linear field dependence at high fields. Furthermore, as the temperature increases beyond the critical temperature $T_{\min}$, the MR becomes much smaller and only the quadratic behavior is observed within the range of magnetic field used in the experiments. For comparison, we also measured the effect of magnetic field applied parallel to the interface ($B_{\parallel}$), and in this case only a small MR was observed at 2 K (**Fig. 3.9b**). This strong anisotropy is in line with the 2D nature of the transport at the LAO/STO heterointerface [114-115].

Figure 3.9 (a) Out-of-plane magnetoresistance measured for various gate voltages at 5 K. (b) Out-of-plane magnetoresistance measured at different temperatures for a fixed $V_g = 0.8$ V. For comparison, typical in-plane magnetoresistance measured at 2 K is also plotted.

On the side, we should note that besides the inhomogeneities, the anomalous linear MR can also arise when the system is in the quantum limit [116], which was reported for materials such as Bi_2Te_3 [117] and multilayer graphene [118]. In the quantum limit, most of the carriers occupy the lowest Landau level, which in general implies a low carriers density (n) and a small effective mass (m^*). In our case, the linear MR is observed at a carrier concentration of $\sim 1 \times 10^{13} \text{ cm}^{-2}$, and if we assume the effective mass to be $\sim 0.7 m_e$ (m_e is the bare electron mass) [32], then the quantum limit can only be reached at a magnetic field of 40 T [116]. However, as

shown in **Fig. 3.9** in our case, the linear MR is observed even at low fields of 1~2 T, which indicates that the scenario of quantum limit is not applicable here.

Figure 3.10 Characterization of the classical linear magnetoresistance. The slope of the linear part of MR (right side) and the inverse crossover magnetic field, $1/B^*$ plotted (left side) as a function of the inverse temperature, $1/T$. Inset shows the definition of the crossover magnetic field, B^* .

Furthermore, we derived the slope dMR/dB of linear MR part and crossover magnetic field B^* between the quadratic and linear dependence of MR from the data in **Fig. 3.9b** to confirm the inhomogeneous character of the electron gas near the insulator-metal transition. The definition of the crossover magnetic B^* is shown in inset of **Fig. 3.10**. In the classical inhomogeneous model, both dMR/dB and $1/B^*$ should show the same temperature dependencies, proportional to $1/T$, due to the thermal excitation [113]. This consistency between them is confirmed as shown in

Fig. 3.10, which further confirms the inhomogeneous character of the electron gas at the LAO/STO heterointerface near the transition.

Consequently, now we are able to conclude that the 2D transport at the LAO/STO interface has a nature of percolation transition due to the disorder potential which cannot be completely screened when the carrier density of the electron gas at the interface is low.

3.4 Electrostatic tuning of Kondo effect

3.4.1 The Kondo effect

The Kondo effect manifested itself, originally in metal, in the form of the abnormal upturn of the resistance (i.e. there is a resistance minimum in the R-T curve.), rather than saturation as normal expected due to the static defects, at low temperatures [119]. No satisfactory explanations for this phenomenon were proposed for almost three decades until Kondo's model in 1964 [119]. The model ascribes the resistance upturn to the scattering process dominated by the weakly interaction between the local magnetic moments from magnetic impurities and the conduction electrons at low temperature. This gives a quantitative interpretation of the logarithmic behavior of the resistance upon the temperature at certain finite temperature range, but fails to explain the saturated-trend behavior at further lower temperatures. Later, with the development of the theoretical methods and the experimental techniques in the past decades, a more comprehensive scenario for the Kondo effect has been established

for the whole temperature range [120-122]. Until now, Kondo effect has been one of the most studied, well understood problems in solid state physics.

In Kondo model, the upturn behavior of resistance requires an antiferromagnetic exchange interaction $\mathbf{J}$ between the localized spin and conduction electrons. This coupling leads to the scatterings of conduction electrons near the Fermi level and hence results in an $\ln T$ contribution to the resistance according to the perturbation calculation. However, this calculation doesn't work at the low temperature range since the resulted resistance from the percolation model will diverge as T approaches certain temperature point, which is not consistent with the experimental observation—a saturation trend once approaching zero temperature. Actually the temperature point where the resistance divergence happens is known as Kondo temperature, T_K , which is an important characteristic energy scale in the discussion of the Kondo problem. Now, it has been well known that below T_K , the coupling between the localized spin and the itinerant electrons is quite strong so as to screen the local magnetic moment completely, as shown in **Fig. 3.11**, forming a many body spin singlet state and making it act like a non-magnetic impurity. Consequently, this strong coupling in the low temperature range also invalidates the perturbation calculation used in the original Kondo model. At this temperature range ($T < T_K$), the spin singlet plays the role as effective scattering centers due to the extended size of the bounding state, therefore resulting in the decrease of the conductance, however, with saturation trend. The transport behavior at this temperature range has been proved to be consistent with the Fermi liquid theory and can be modeled as

$$\rho(T) = \rho_0 \left\{ 1 - c \left(\frac{T}{T_K} \right)^2 \right\} \quad (3.3)$$

where the c is constant and ρ_0 is the Kondo resistance at zero temperature. As shown in the model, the resistance only depends on the temperature divided by the Kondo temperature. According to the numerical renormalization group (NRG) theory [122], this single scaling behavior can be extended to a wider temperature range, even above T_K . As a result, an empirical model for the temperature dependent transport behavior in a wider temperature range, including the range below and above T_K , has been proposed [123-125], which can be used to confirm the Kondo origin of the transport properties in certain systems and will be introduced in the following section.

Figure 3.11 Schematic of a spin singlet state (shaded area) between the localized spin (red arrow) and the spins of the conduction electrons (black arrows).

3.4.2 Experimental results

In this section I will address the transport behavior in the high gate regime, where, $T_{\min}$ intriguingly increases with the gate voltages and equivalently the carrier density (**Fig. 3.5**). As shown in **Fig. 3.12**, detailed R_s -T data with progressively increasing gate voltages were collected on the device LS-3, and the focus is on the high voltage regime where anomalous resistance upturns emerge at low temperatures. The enhancement of the resistance upturn at higher gate voltages (equivalently higher carrier density) allows us to exclude the weak localization and the electron-electron interaction as the dominating mechanism in the low-temperature transport [101,126]. At higher carrier densities, the weak localization and electron-electron interaction should be suppressed, and so should the resistance upturn, which is, however, contrary to our observation. An alternative mechanism which can cause the low-temperature resistance upturn in metallic systems is the Kondo effect, which arises from the interplay between the itinerant conduction electrons and the spins of localized magnetic centers [119,122], as introduced in last section. The positive correlation between the magnitude of the resistance upturn, defined by the depth of the upturn in the temperature dependence of relative resistance $R_s(T) - R_s(2\text{K})$, and the carrier density n_s , as shown in the inset of **Fig. 3.12**, is consistent with the characteristics of the Kondo effect.

Figure 3.12 Temperature dependent sheet resistance of the device LS-3 measured at various gate voltages. Inset shows the plot of the normalized sheet resistance ($R_s(T) - R_s(2K)$) versus the temperature.

As introduced in the last section, according to the numerical renormalization group (NRG) method, the electrical resistance contributed by the Kondo effect shows a universal behavior as function of a single scaling parameter T/T_K [122], which is often taken as a key criterion to verify the Kondo scenario. Accordingly, we fit our transport data (R_s vs. T) using [123,125]

$$R_s(T) = R_0 + aT^b + R_K(T/T_K) \quad (3.4)$$

$$R_K(T/T_K) = R_{K,0} \left(\frac{1}{1 + (2^{1/s} - 1)(T/T_K)^2} \right)^s \quad (3.5)$$

In the equation (3.4), R_0 is the residual resistance, presumably originating from impurity scatterings that do not necessarily involve the spin degree of freedom; the

second power-law term is the general expression of transport [127], which may involve electron-electron and electron-phonon contributions; in the third term, $R_K(T/T_K)$ is an empirical function for the universal Kondo transport, and $R_{k,0}$ is the Kondo sheet resistance at zero temperature. In the equation (3.5), the parameter s is fixed at 0.225 for $S = \frac{1}{2}$ systems [123]. **Figure 3.13** show a typical fitting result for the device LS-3 at $V_g = 3.5$ V, which verifies the Kondo scenario.

Figure 3.13 Sheet resistance R_s measured at a particular gate voltage $V_g = 3.5$ V in the temperature range of 2 to 50 K. The red solid line is fitting to the transport data to the Kondo scenario according to the Equation (3.4) and (3.5).

Figure 3.14 presents the data of the normalized sheet resistance versus the reduced temperature measured for different gate voltages. The data points collapse into a single curve, which is consistent with the universal transport behavior

predicted by the NRG calculations for the Kondo effect. Deviations show up only at temperatures higher than T_K , which may be caused by other transport mechanisms involving either phonons or activated carriers [124].

Figure 3.14 Plots of the normalized Kondo resistance ($R_K(T)/R_{K,0}$) versus the reduced temperature (T/T_K), where the Kondo temperature T_K varies from 20 to 47 K for various gate voltages. The red solid curve is the universal Kondo transport behavior obtained from the numerical renormalization group (NRG) method.

Figure 3.15 shows the gate-voltage dependence of parameters R_0 , $R_{K,0}$ and T_K derived from fitting the transport data to the universal Kondo model. R_0 , which is caused by the impurity scatterings, decreases monotonically upon the increase of the gate voltage, i.e. the carrier density. On the other hand, the Kondo resistance $R_{K,0}$

Figure 3.15 Gate-voltage-dependent parameters R_0 , $R_{K,0}$ and T_K extracted from the transport fittings.

increases upon the gating, which seems to contradict with the conventional trend expected for systems with fixed concentrations of magnetic spin centers [124]. In the Kondo model, $R_{K,0}$ is proportional to n_m/n_s , where n_m and n_s are the sheet concentration of the magnetic spin centers and the carrier density of the host material [124,128-129], respectively. Since n_s of the LAO/STO heterointerface increases upon the increase of gate voltage, we can deduce that the density of the magnetic spin centers must increase faster with the gate voltage in order to account for the observed gate tuning of $R_{K,0}$. Finally, the Kondo temperature T_K increases from 20 to 47 K upon the increase of gate voltage. We note that the Kondo temperature derived here is lower than the value reported by Brinkman and coworkers [4], which may be a result of different parameters used in the PLD growth. Nevertheless, the

gate-tuning effect implies an electrostatic enhancement of interaction between the conduction electrons and the magnetic centers.

Figure 3.16 (a) Angle-dependence MR with a 7 T field applied at 2 K at $V_g = 3.0 \text{ V}$.

A strong anisotropy was observed. The angle is defined as the one between the normal of LAO/STO interface and the magnetic field direction. (b) In-plane MR measured at various temperatures under $V_g = 3.0 \text{ V}$.

An additional evidence of supporting the Kondo scenario can be provided by studying the transport properties as function of magnetic field in the regime of resistance upturn, as the applied magnetic field will suppress the coupling between the spin-singlet and conducting electrons due to the Zeeman effect and thus result in negative magnetoresistance [122,125]. Accordingly the Zeeman effect of spin character should have no field-orientation dependence, i.e. both the out- and in-plane magnetoresistance should be negative if they are only contributed by this spin effect. However, if there is contribution from the Lorentz force, its contribution to the MR may overlap with the spin-contributed one, or even dominate the MR, which is our

case here as confirmed by the angular-dependence MR in **Fig. 3.16a**, where the negative MR can only be seen near the in-plane (LAO/STO interface) orientation of the field. **Figure 3.16b** shows the negative in-plane MR at various temperature, from which we can see that the negative MR is suppressed when the temperature is high enough. This temperature dependence is reasonable in consideration of the role of the thermal energy, which can suppress the Kondo effect when it is large enough. It's noted that the data shown in **Fig. 3.16** is a typical case in our measurement, which are confirmed in other devices we studied.

To further shed light on the gate-tuned Kondo effect, we also studied the out-of-plane MR at low temperatures, as the observed quantum orbital effect can offer valuable information about the Kondo effect strength. **Figure 3.17** shows the out-of-plane MR of the device LS-1 measured at 2 K in the Kondo regime. Due to the strong orbital effect, the out-of-plane MR shows the positive quadratic dependence on the magnetic field. Remarkably, in the low magnetic field region (inset of **Fig. 3.17a**) the MR exhibits a distinct shape of sharp cusp, which can be ascribed to the weak antilocalization (WAL). In general, WAL arises due to the present of a strong spin-orbit coupling [130], which emerges at the LAO/STO heterointerface due to the broken structural inversion symmetry [19], and its atomic nature as a result of the degenerate d bands [110]. This destructive interference effect of coherently back-scattered electrons enhances the conductivity of the system (more discussion about this can be found in section 4.2). The applied out-of-plane magnetic field suppresses the conduction enhancement and hence results in the sharp increase

of the resistance at low fields, i.e. the observed sharp cusps in the MR data. We modeled the low-field MR according to the Hikami-Larkin-Nagaoka theory [131], from which the phase coherence lengths are deduced. The fitting model is given as [132]

$$\Delta\sigma(B) = -\frac{e^2}{2\pi^2\hbar} \left[\psi\left(\frac{1}{2} + \frac{B_1}{B}\right) - \frac{3}{2}\psi\left(\frac{1}{2} + \frac{B_2}{B}\right) + \frac{1}{2}\psi\left(\frac{1}{2} + \frac{B_\phi}{B}\right) + \ln\left(\frac{B_2^{3/2}}{B_1 B_\phi^{1/2}}\right) \right] \quad (3.6)$$

where $\psi(x)$ is the digamma function and

$$\begin{aligned} B_1 &= B_e + B_{s.o.} + B_s \\ B_2 &= B_i + \frac{4}{3}B_{s.o.} + \frac{2}{3}B_s \\ B_\phi &= B_i + 2B_s \end{aligned}$$

The characteristic field B_n represents the different electron scattering processes involved, where i, e, s.o. and s stand for the inelastic, elastic, spin-orbit and magnetic scattering processes, respectively. The phase coherence length l_ϕ is obtained from the extracted B_ϕ through the following equation

$$l_\phi = \sqrt{\hbar/4eB_\phi} \quad (3.7)$$

A typical fitting at $V_g = 3.0$ V is shown in **Fig. 3.17b**. The phase coherence length, l_ϕ are deduced as 91.5, 90.8 and 61.8 nm for $V_g = 2.5$, 2.6 and 3.0 V, respectively (listed in **table 3.1**). The decrease of the phase coherence length upon increasing gate voltage indicates the enhanced phase-breaking interaction between the conduction electrons and the scattering centers. As the low-temperature transport is dominated by the Kondo effect, this effect can be attributed to the enhancement of

the magnetic spin scattering at higher gate voltages, which supports the tuning of the Kondo effect by the electrostatic field.

Figure 3.17 (a) Out-of-plane MR at 2 K for various high gate voltages. Inset shows the enlarged view of MR in the low magnetic field region. (b) Normalized magnetoconductance measured at $V_g = 3.0$ V. The red solid line is fitting to the Hikami-Larkin-Nagaoka theory. Data here were obtained from LS-1.

Table 3.1 The extracted characteristic magnetic field and phase coherence length.

V_g (V)	2.5	2.6	3.0
B_ϕ (mT)	19.6	19.9	43.0
l_ϕ (nm)	91.5	90.8	61.8

3.5 Discussion and summary

Overall, by examining two separate transport regimes at different gate voltages, our EDLT experimental results shed new light on the physical properties of LAO/STO

heterointerface. Within the accessible ranges of temperature and gating, resistance upturn persists in transport, which is expected for 2DEG with localization of electrons [102]. The transition of the transport behaviors and the emergence of the Kondo effect at a carrier density of $\sim 1.69 \times 10^{13} \text{ cm}^{-2}$ suggest that the successive filling of electrons in different Ti 3d orbitals lies behind the observed phenomena. At the LAO/STO interface, the orbital reconstruction due to the broken symmetry is well established both theoretically [64,83] and experimentally [33,133]. In particular, the degeneracy of the Ti t_{2g} states is lifted at the interface, and the Ti $3d_{xy}$ states possess the lowest energy, and consequently the $3d_{xy}$ -derived band is occupied first, but these electrons are highly susceptible to localization. As a result, we observed in the low-gate regime the significant role of inhomogeneity, and the field-induced insulator-to-metal transition in the LAO/STO heterostructures exhibits a clear nature of 2D percolation transition.

There may be several possible origins behind the often observed disorders and random potentials. Because of the strong spin-orbit coupling at the LAO/STO heterointerface and the perpendicular electric field, multiple factors of instability towards phase separation may be present at the interface [91]. Furthermore, inhomogeneities with different scales and strength may also originate from extrinsic synthesis-related sources such as terrace steps, incomplete coverage of the LAO layer, local nonstoichiometry in composition, structural dislocations, ionized defects, impurities, and so on. Thus, it remains as a challenge to quantitatively reconcile the experimental results reported in literatures. On a related aspect, it is recently

proposed that the imperfectly ordered ions at the electrolyte-oxide interface in an EDLT structure could generate inhomogeneous electric fields and thus result in inhomogeneities in the conducting channel [134]. In addition to the usually expected electrostatic effect, ionic liquid gating may induce electrochemical reactions at the channel surface [100] and dynamic migration of oxygen vacancies [135]. Completely excluding these effects requires extensive experiments carried out under carefully controlled measurement environments.

Here, we should note that the LAO layer, although very thin, contributes to the robustness of the channel in the EDLT devices. We measured multiple devices and the results are highly reproducible. In a control experiment, we used a bare LAO substrate as the channel and did not observe any gating effect. Although we cannot completely exclude the electric-field-induced migration of oxygen at the interface between the ionic liquid and the oxide channel [135], the LAO layer serves as a barrier for suppressing such electrochemical effects. In addition, atomic force microscopy (AFM) experiments after the EDLT experiments showed no change of the sample surface, indicating that LAO is chemically stable. Thus, it is reasonable to conclude that the gating effect we observed herein is not a result of modified LAO layer; instead it should be attributed to the electric-field-induced electronic modification of the heterointerface.

It is insightful to compare our results with the reports in literatures on EDLT devices with bare STO substrates as the channel [96,125,134,136]. The critical carrier densities in those devices for the onset of metallic channel transport vary

between 10^{13} and 10^{14} cm^{-2} [96,134,136]. In contrast, when oxide and polymer dielectrics were used as the gate insulator, high-mobility transport was observed in the STO channel at much lower carrier densities on the order of 10^{12} cm^{-2} [137-138]. This difference may be attributed to electrochemical interaction and high trap density at the STO/electrolyte interface. Moreover, in the electrolyte-gate STO experiments, the threshold voltages to induce insulator-to-metal transition are over 1.5 V [96,134], which is much higher than 0.4 V we observed in our devices. Since the device configurations and experimental conditions are similar, this difference in threshold voltage should be ascribed to the presence of three u.c. LAO and the built-in field in the layer.

In our EDLT experiments, the applied electric field can effectively control the transport properties of heterointerfaces by modulating the density and distribution of electrons in different sub-bands [19,44,92-93,110,139]. The resistance upturn in the low-gate regime does not come from the Kondo scattering. Only after the electron density reaches a critical value of $\sim 1.69 \times 10^{13} \text{ cm}^{-2}$, where the electrons are probably distributed into different $3d$ -orbital-derived bands and the electron density is well above the critical percolation threshold, the Kondo effect emerges. From the extracted parameters in the Kondo fitting and the magneto-transport measurements, it is clear that the applied electric field can effectively tune the coupling between the magnetic centers and the conduction electrons. The concentration of Kondo magnetic centers can be estimated from the Kondo screening model at the $T \rightarrow 0$ limit, i.e.,

$$R_{K,0} \approx \frac{h n_m}{\pi e^2 n_s} \quad (3.8)$$

where n_m and n_s are the sheet concentrations of magnetic centers and conduction electrons at the heterointerface, respectively [124,129]. Accordingly, we estimate that the concentration of magnetic centers n_m in the Kondo regime is on the order of 10^{12} cm^{-2} , i.e., 10^{-3} per perovskite u.c., which is much lower than the density of itinerant electrons and in line with the requirement of Kondo scenario. This low concentration of magnetic centers is also consistent with the weak magnetism directly measured at the LAO/STO interface [5,88]. In fact, it was proposed recently that only a small fraction of the total paramagnetic moments, which may come from charge ordering or oxygen vacancy mechanism [89-90], are coupled to the itinerant electrons, serving as scattering centers.

In summary, we investigated EDLT with the top-gate configuration using the insulating LAO/STO heterointerface as the channel, and we found that the electrostatically induced insulator-to-metal transition has a nature of inhomogeneous percolation transition. Even at the highest gate voltage, a resistance upturn persists at the low temperatures, which can be attributed to the Kondo effect with a magnetic origin. Our results shed new light on the intriguing electronic and magnetic properties of the LAO/STO heterostructures, and the insight on the evolution of 2D electrons under the electrostatic modulation may eventually lead to the construction of novel oxide electronics with optimal performance.

Chapter 4

Study of spin-orbit interaction in asymmetric oxide heterostructures

4.1 Introduction

The relativistic spin-orbit interaction (SOI) couples the spin degree of freedom of electrons with the orbital environments [140]. This entanglement not only plays essential roles in a flurry of condensed matter phenomena, such as spin Hall effect [141-142], topological insulator [143] etc., but also underlies the potential applications of spintronic devices [144-146]. Besides metals and semiconductors, exploration of SOI has recently been extended to oxide heterostructures [19,147] and oxides with heavy elements [148-149]. As introduced in chapter 1, because of the strong correlation between multiple degrees of freedom [12,81], rich physics is expected in oxide interfaces. The demonstration of the SOI in LAO/STO heterostructure as well as superconductivity and magnetism at the interface leads to envisage of exotic properties [46,150-152]. The spiral and skyrmions phase is expected as a result of the interplay between magnetization and SOI [46,151]. The possibility of topological superconductivity is proposed for interacting Rashba bilayers due to the co-existence of superconductivity and SOI [152]. In respect to the potential applications in oxide electronics, the intrinsic spin Hall effect may exist at oxide interfaces with large SOI [150]. However, these concepts are still in the

embryonic stage, and so far the tuning of SOI in oxide heterostructures has relied on the application of external gate bias in field effect devices. The prerequisite for experimental realization of SOI-related exotic properties is the development of reliable and universal approaches to control the SOI in oxide heterostructures.

Figure 4.1 Schematic diagram of the asymmetric $\text{LaAlO}_3/\text{SrTiO}_3/\text{LaAlO}_3$ oxide heterostructure, where n interface means the $\text{TiO}_2\text{-LaO}$ one with conductivity and p interface is the insulating one with $\text{AlO}_2\text{-SrO}$.

In this chapter, we investigated the magnetotransport and the weak antilocalization (WAL) effect in a new type of ultrathin oxide heterostructure, namely LAO/STO/LAO oxide heterostructures with inequivalent termination layers at the two interfaces, as shown in **Fig. 4.1**. We discovered that the strength of SOI in such asymmetric heterostructures can be modulated by the thickness of the inserted STO layer. The mechanism behind the tuning of SOI is ascribed to the built-in electric field in the STO layer, which is verified by the observation of a notable electrostrictive effect.

4.2 Spin-orbit interaction in oxide heterostructure

4.2.1 The brief introduction of the spin-orbit interaction

In quantum physics, the spin-orbit interaction is an interaction of a particle's spin with its motion. The motion of an electron with a velocity, $\mathbf{v}$, in an electric field, $\mathbf{E}$, will experience a magnetic field in the rest frame:

$$\mathbf{B}_{\text{eff}} = \gamma (\mathbf{v} \times \mathbf{E})/c^2 \quad (4.1)$$

where c is the speed of light and γ is a factor, which can be taken as 1 in practical cases. Like the Zeeman's coupling, this internal field can interact with the spin of the moving electron itself, resulting in

$$H_{\text{SOI}} = \frac{\mu_{\text{B}}}{2c^2} (\mathbf{v} \times \mathbf{E}) \cdot \boldsymbol{\sigma} \quad (4.2)$$

where $\boldsymbol{\sigma}$ represents the Pauli spin matrices and μ_{B} is the Bohr magneton. On the other hand, if we regard the approximation of the electric field (V) as spherically

symmetric one, the energy term can also be written in the form with the terms of orbital and spin angular momentum (**L** and **S**) involved

$$H_{\text{SOI}} = \frac{\mu_B}{2mc^2} \left(m\mathbf{v} \times \left(-\frac{1}{\epsilon} \frac{\mathbf{r}}{r} \frac{dV}{dr} \right) \right) \cdot \boldsymbol{\sigma} = \frac{1}{2m^2 c^2} \frac{1}{r} \frac{dV}{dr} (\mathbf{S} \cdot \mathbf{L}) \quad (4.3)$$

This is also called atomic SOI, which contributes to the hydrogen fine structure. In solid matter, it can also lift the band degeneracy in certain conditions, such as the splitting of 3d t_{2g} of Ti in STO bulk as introduced in chapter 1. However, though being with $\mathbf{B}_{\text{eff}}$, the spin degeneracy of each band is preserved in most bulk systems with the centrosymmetric structure, i.e. $E(\mathbf{k}, \uparrow) = E(-\mathbf{k}, \uparrow)$, where the $\mathbf{k}$ is wave vector and $\uparrow$ ($\downarrow$) denotes the state with spin up (down). This is attributed to an extra symmetric restriction—time reversal symmetry with $E(\mathbf{k}, \uparrow) = E(-\mathbf{k}, \downarrow)$. (From the two energy equations above, we have $E(\mathbf{k}, \uparrow) = E(\mathbf{k}, \downarrow)$, i.e. spin degeneracy)

On the other hand, according to the discussion above, the spin degeneracy will be lifted once one of the symmetries is broken. The external magnetic field, for example, breaks the time reversal symmetry and hence lifts the spin degeneracy, i.e. the Zeeman Effect. Alternatively, in presence of the time reversal symmetry (zero magnetic field), the spin degeneracy can also be lifted through breaking the structure inversion symmetry. Normally the systems with inversion asymmetry are classified into two groups:

- **Bulk inversion asymmetry (BIA)**, happens in a system that lacks symmetry under reflection about a plane that contains at least one lattice site in the underlying crystal. These systems are known as

non-centrosymmetric crystals, including the materials with Zinc-blendes structure or Wurtzite structure.

- **Structure inversion asymmetry (SIA)**, normally happens on the surface of metals, asymmetric quantum wells, interfaces of heterostructure, or 2D systems with the symmetry-breaking electric field in out-of-plane direction. The spin-orbit interactions at these systems are normally called Rashba effect.

Figure 4.2 (a) Energy spectrum of the 2D free electron gas split by the Rashba spin-orbit interaction. (b) and (c) show the schematic spin configurations on the Fermi contour due to the linear and cubic Rashba effect, respectively. (a) from Ref. [141]

Rashba effect

The Rashba effect was initially proposed by E. I. Rashba based on the ideal free electron model and describes the SOI in quasi-2D free electron gas, [153]. According to this model, an electron with only in-plane momentum $\mathbf{p}$ experiences an effective magnetic field derived from the electric field due to the confined potential in the direction normal to the electron gas plane ($\mathbf{z}$ direction), i.e. $\mathbf{E} = \nabla V = dV/dz \mathbf{e}_z$, where $\mathbf{e}_z$ denotes the unit vector in the z direction. As a result, the gradient potential (or extrinsic perpendicular electric field) critically determines the effective magnetic field and hence SOI. This leads to the spin-orbit Hamiltonian in the form of

$$H_{\text{SOI}} = \alpha(\mathbf{e}_z \times \mathbf{p}) \cdot \boldsymbol{\sigma} \quad (4.4)$$

where α is a factor which is proportional to the gradient potential experienced by the electron in $\mathbf{z}$ direction. Consequently, the Rashba effect results in the energy splitting of the originally spin-generated parabolic band, shown in **Fig.4.2a**, and the splitting energy is proportional to the wave vector either linearly or in cubic (named as linear Rashba term and cubic Rashba term, respectively), depending on the nature of the band occupied by the electrons [140,154-155]. The other feature is that the directions of the spin of the electrons will have certain relationship with the direction of their own orbital moments, as shown in **Fig. 4.2b** and **c**.

4.2.2 Characterization of the spin-orbit interaction by magnetotransport measurement

The SOI in two dimensional electron systems can be detected by multi methods, one of which is the measurements of transport properties under extra magnetic field. It is also the one used in this chapter and will be briefly introduced in this section. This method works for a system exhibiting the quantum conduction correction at low temperatures, which is due to the quantum effect of the diffusive electron in the system. The resulted weak localization effect (WL) in such systems is easily influenced by the SOI, in turn providing an effective way to detect the strength of the SOI based on the well-developed theoretical models.

According to the classical Boltzmann theory, the conductivity of a free electron is given by the Drude formula $\sigma = \frac{ne^2}{m} \tau_0$, where n is carrier density, m the electron mass and τ_0 elastic lifetime of the free electron. In this theory, the eigenstate of momentum of the electron is conserved. In such a model, no interference between electron waves is considered, which works well for simple metals, especially at high temperatures. In other words, no substantial interference between electron waves can be established before the energy-losing interactions of the electrons, such as electron-phonon interaction, occur to destroy the phase coherence between the waves. Here the lifetime between energy-losing scatterings is called inelastic lifetime τ_i . On the other hand, if the inelastic lifetime is long enough, far larger than the elastic lifetime, the phase coherence between electron waves can last long enough to have multi elastic scatterings before the inelastic scattering happens, which is the regime

where the weak localization effect may occur. However, not all the interfering electron paths can finally have influences on the conductance of these diffusive systems.

Figure 4.3 (a) the typical multi-scattering events considered in weak localization scenario; (b) the typical magnetoresistance for weak localization (WL) effect and weak anti-localization (WAL) effect. The case shown here is taken from Ref. [132], where the gold (Au) was purposely doped into the magnesium (Mg) to introduce the spin-orbit interaction in the system.

In the scenario of weak localization, the electron paths with closed loops are considered, as shown in **Fig. 4.3a**, in which the electron returns to the start point after a series of elastic scattering events. And the two paths with opposite directions of precessions (i.e. the red and blue paths in **Fig. 4.3a**) can be executed with the same probabilities. Another premise of this scenario is that among the scattering events occurring in these electron trajectories, no inelastic scattering is involved. Therefore, a constructive interference between the electron waves of these two paths

is resulted, due to the identical lengths and scattering events they experience, but, in opposite directions. Such a constructive interference enhances the probability of these back-scattering processes. Compared to the classical transport theory, this adds additional negative conductance to the classical one of the electrons, namely the quantum conduction correction effect, and eventually leads to the divergent of the conductance of the systems at zero temperature. Nevertheless, this constructive interference can be destroyed by the application of an external magnetic field, as it can shift the phases of the two associated waves with opposite signs to make them out of phase at certain strength. Collectively, this results in a negative magnetoresistance in term of transport properties, which in turn provides an important way to study the WL effect in such diffused systems, as shown in **Fig.4.3b**.

The SOI effect can generate an effective magnetic field and thus flip the spin of an electron as the electron proceeds in the momentum space, as introduced in last section. Consequently the SOI can destroy the constructive interference and even lead to the destructive interference between the electron paths to suppress the back-scattering process of electrons, thus resulting in a positive contribution to the conductance of the system. In such a scenario, an external magnetic field will suppress the destructive interference and thus decrease the conductance, as shown in **Fig.4.3b**. The effect by SOI is opposite to the WL effect and therefore named as weak anti-localization (WAL) effect.

These scenarios have been well studied theoretically in the last three decades

[101,132], which enables us to quantitatively simulate the measured magnetoconductance data to get the critical physical parameters, such as the spin relaxation length of electrons, which characterizes the strength of the SOI in the system. And this is the fundamental physics, of which we make use to investigate the tuning of the SOI in our artificial asymmetric oxide structures. For the model we used, it will be introduced in the context of the experimental results.

4.3 The Preparation of the asymmetric oxide heterostructure of $\text{LaAlO}_3/\text{SrTiO}_3/\text{LaAlO}_3$

To ensure the asymmetric structure with the n and p type interface on either side of the STO well, every LAO substrate used for growth is treated to have the AlO_2 termination according to the method introduced in chapter 2 and confirmed by the AFM scanning, as shown in **Fig. 4.4**. And the *in situ* precise monitoring of the film thickness by the RHEED enables us to deposit the proper thickness of the STO layer to have TiO_2 termination and thus the n type interface with the capping LAO layer. All the films were grown at 800 °C under pressure of $\sim 1 \times 10^{-6}$ mbar and with the laser energy at $\sim 1 \text{ J/cm}^2$ on AlO_2 -terminated LAOs. Before the deposition of the STO, a 10 unit cell (uc) LAO buffer layer was deposited to ensure the quality of the interface with STO. Then a STO layer with controlled thickness was deposited to produce a series of asymmetric oxide heterostructure, followed by the deposition of 10 uc LAO top layer. The layer-by-layer growth mode was maintained as indicated by the periodic RHEED oscillation (**Fig.4.5a** for a typical heterostructure with 15 uc

inserted STO). **Figure 4.5b** shows the RHEED patterns at various growth stages of the heterostructure. After growth finishing, the AFM was used to have the topography image to check the quality of the film. The typical image is shown in **Fig.4.6a** for the structure with LAO/STO/LAO (10/15/10 uc). To further confirm the quality of the structures, the X-ray reflectivity (XRR) experiments were carried out, and the observed obvious oscillation in **Fig. 4.6b** indicates the sharpness of the interface of the structure grown. From the simulation of the reflectivity (red curve of **Fig.4.6b**), we can obtain the thicknesses of each layer of the structure, which are consistent with the ones from the RHEED oscillation.

Figure 4.4 AFM topography images for the LaAlO_3 substrates after treatment, where the Ra represents the surface roughness in unit of Angstrom. (Scan area: $3 \times 3 \mu\text{m}$)

Figure 4.5 (a) RHEED oscillation during the film deposition for LAO/STO/LAO (10/15/10 uc) heterostructure. (b) shows the RHEED reflected patterns at various stages of heterostructure growth.

Figure 4.6 (a) AFM topography images and LAO/STO/LAO (10/15/10 uc) films, whose area is $3 \times 3 \mu\text{m}$. (b) X-ray Reflectivity measurement for the same film. The circle symbols correspond to the experimental data and the red curve the simulation.

4.4 Tuning spin-orbit interaction in heterostructure of $\text{LaAlO}_3/\text{SrTiO}_3/\text{LaAlO}_3$

We further performed high resolution X-ray theta-2theta measurements on the heterostructures to detect the variation of out-of-plane lattice constant, as shown in **Fig. 4.7a**. The out-of-plane lattice constant c of the STO layer was determined by fitting to the fringe oscillations (the inset of **Fig. 4.7b** shows the typical fitting result of the LAO-STO-LAO structure with 10 uc STO layer), and interestingly, we found that c increases from 3.895 to 3.946 Angstrom ($\text{\AA}$) in the series of heterostructures (**Fig. 7b**). We can exclude the compressive strain from the LAO substrate as the main cause of this variation of the STO lattice parameter. For such ultrathin films, the strain state as a result of lattice mismatch should remain constant, and the c value was reported to be 3.96 $\text{\AA}$ for a 40 uc STO film prepared at similar conditions but without the LAO capping layer [77]. This means that besides the elastic deformation due to the LAO substrate, there exists an extra stress that compresses the STO layer in the out-of-plane direction. If this thickness dependent variation of c was caused by the relaxation of STO layer, the opposite trend would be expected; so does the interdiffusion, which would elongate the out-of-plane lattice constant of STO near the interface [68]. More importantly, the value of c closely follows the quadratic relationship with the STO thickness, as shown in **Fig. 4.7b**, which invokes the electrostrictive effect in the STO layer, analogous to the observation made in LAO/STO heterostructures [156].

Figure 4.7 (a) Theta-2theta measurements around [002] peak of the LAO substrate for the LAO/STO/LAO oxide well with variant inserted STO thickness. (b) Calculated out-of-plane lattice constant *c* from simulation as function of thickness. Inset shows the typical fitting for the data of oxide well with 10 uc STO inserted.

Hall effect measurement confirmed that the transport properties in these asymmetric heterostructures were dominated by their *n* type interface as designed. In such heterostructures, both the electrons from the *n* type interface and those doped by the oxygen vacancies may contribute to the conduction. If the carriers were mainly introduced by the oxygen vacancies in semiconducting doped STO, the sheet carrier concentration, n_b , with a bulk origin, would be proportional to the STO thickness. However, we found that the sheet carrier concentration n_H , calculated from the Hall effect measurements, monotonously increases from $1.07 \times 10^{14} \text{cm}^{-2}$ to $1.92 \times 10^{14} \text{cm}^{-2}$ on decreasing STO layer thickness, as shown in **Fig. 4.8a**. This observation excludes the oxygen vacancy related n_b as the dominant source of conducting carriers. This conclusion is further confirmed by a control

experiment carried out on an amorphous $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_7$ (LSMO)/LAO/STO structure which was prepared under the same condition as the LAO/STO/LAO heterostructures except that the top LSMO layer was deposited at room temperature. The absence of measurable conductivity in such a-LSMO/STO/LAO structure indicates that the electrons introduced by the oxygen vacancies cannot be responsible for the conduction of the heterostructures. Thus, the top LAO/STO interface is indispensable to achieve a measurable level of conduction in such oxide heterostructures [157].

Figure 4.8 (a) The thickness dependent sheet carrier density measured on the LAO/STO/LAO heterostructures. The solid line is the fitting to the phenomenological model of two parallel transport channels with separate interface and bulk related origins. (b) Schematic band diagram of the LAO/STO/LAO heterostructure with asymmetric interfaces and built-in field.

To elucidate the nature of transport in such asymmetric heterostructures, we considered a phenomenological model [158-159] involving both the n type LAO/STO interface and the doped STO layer as two parallel conducting channels.

Then the sheet carrier concentration n_H and the mobility μ_H derived from the Hall effect measurement can be written as follows:

$$n_H \mu_H = n_i \mu_i + n_b \mu_b \quad (4.5)$$

$$n_H \mu_H^2 = n_i \mu_i^2 + n_b \mu_b^2 \quad (4.6)$$

where n_i is the interface sheet carrier density, being thickness independent, and n_b accounts for the sheet carrier density of the doped STO layer. The thickness dependent $n_b = ncd$, where n is the bulk carrier density of semiconducting STO, c is the out-of-plane lattice constant, and d is the number of unit cell of the STO layer.

As shown in **Fig. 4.8a**, this simple model gives good fitting to the experimental carrier concentration data. The derived parameters $n_i = 4.1 \times 10^{14} \text{cm}^{-2}$, which is close to the theoretical value ($3.5 \times 10^{14} \text{cm}^{-2}$) expected for the LAO/STO heterointerface in the polar catastrophe model [64]. On the other hand, the bulk carrier density $n = 1.2 \times 10^{19} \text{cm}^{-3}$ is two orders of magnitude lower than the value reported for epitaxial STO films prepared on STO substrates [160]. This discrepancy may be ascribed to strains and disorders in the STO layer when it is grown on substrate with lattice mismatch [157]. The sheet carrier density n_s with the bulk origin is from 10^{12} to 10^{13}cm^{-2} , e.g., for 10 uc STO in heterostructures, $n_s = 4.8 \times 10^{12} \text{cm}^{-2}$, which is far smaller than the interface sheet carrier density n_i . Thus, we can conclude that the charge-transfer interface carriers dominate the conduction of the channel in such asymmetric heterostructures.

In **Fig. 4.8b**, we draw the schematic band diagram of the heterostructure, where the carriers are mainly located at the n type interface, and the ensuing asymmetry

produces a build-in electric field within the STO layer.

Figure 4.9 (a) Magnetoresistance measured on the LAO/STO/LAO (10/30/10 uc) heterostructure at various temperatures. The temperature dependent cusp and shift of the peak position indicate the presence of strong SOI. (b) MR at 2 K for the LAO/STO/LAO oxide well with variant inserted STO thickness.

As the phase coherence of the quantum correction to the conductance, including weak localization (WL) and weak anti-localization (WAL), is sensitive to an external magnetic field (introduced in section 4.2.2), magnetotransport can provide insight on the nature of SOI in oxide heterostructures [132]. **Figure 4.9a** shows the magnetoresistance (MR) of the asymmetric heterostructure with 30 uc STO inserted between the LAO layers. The negative MR at 20 K and 30 K is a signature of WL, while on decreasing temperature a cusp emerges around the zero field and broadens progressively. Such MR features at low temperatures are manifestations of WAL, indicating the presence of strong SOI in the systems [161-163].

By varying the thickness of the STO layer in the heterostructures, we can systemically tune the magneto-transport and SOI. As shown in the 2 K MR data in

Fig. 4.9b, the zero-field cusp shrinks on increasing STO layer thickness, and finally negative MR emerges at the high magnetic field at the thickest STO layer of 60 uc. This indicates a crossover from the WAL to the WL regime with the increase of STO thickness, i.e. from the SOI dominated regime to the inelastic scattering dominated regime (WL), therefore reflecting the significant modulation of the SOI in the heterostructures [19,164-165].

Figure 4.10 Fitting (lines) of the magnetoconductance data (symbols) to the ILP model.

To quantify the modulation of the SOI upon the change of the STO layer thickness, we adopted the model developed by Iordanskii, Lyanda-Geller, and Pikus (ILP) to analyze the magnetotransport data [148,166-167]. This model involves two spin-splitting energy terms due to different k -dependent spin-precession vectors.

Such magnetotransport properties are in line with the $3d_{xy}$ and $3d_{xz/yz}$ nature of Ti orbital in SrTiO_3 interface/surface systems as suggested by recent calculations [154-155]. Our Hall effect measurements suggest that the sheet carrier density of the LAO/STO/LAO heterostructures is on the order of 10^{14} cm^{-2} , which is much higher than the universal carrier density of $-1.68 \times 10^{13} \text{ cm}^{-2}$ measured at the LAO/STO interface [110]. When the Lifshitz transition occurs, the $3d_{xz/yz}$ bands start to be populated at the LAO/STO interface with the $3d_{xy}$ already populated. The full equation of the ILP model with contribution from $B=0$ removed is [166]:

$$\Delta\sigma(B) - \Delta\sigma(0) = \frac{e^2}{4\pi^2\hbar} \left[\frac{1}{a_0} + \frac{2a_0 + 1 + \frac{B_{SO1}}{B} + \frac{B_{SO3}}{B}}{a_1(a_0 + \frac{B_{SO1}}{B} + \frac{B_{SO3}}{B})} - \sum_{n=1}^{\infty} \left\{ \frac{3}{n} - \frac{3a_n^2 + 2a_n(\frac{B_{SO1}}{B} + \frac{B_{SO3}}{B}) - 1 - 2(2n+1)\frac{B_{SO1}}{B}}{(a_n + \frac{B_{SO1}}{B} + \frac{B_{SO3}}{B})a_{n-1}a_{n+1} - 2\frac{B_{SO1}}{B}[(2n+1)a_n - 1]} \right\} + \right. \\ \left. \Psi\left(0.5 + \frac{B_\phi}{B}\right) \right] + \frac{e^2}{2\pi^2\hbar} \left[-0.5 \ln \frac{B_\phi}{B} + \ln \frac{B_\phi + B_{SO1} + B_{SO3}}{B} + 0.5 \ln \frac{B_\phi + 2B_{SO1} + 2B_{SO3}}{B} \right] \quad (4.7)$$

where

$$a_n = n + \frac{1}{2} + \frac{B_\phi}{B} + \frac{B_{SO1}}{B} + \frac{B_{SO3}}{B} \quad (4.8)$$

B_{SO1} , B_ϕ and B_{SO3} refer to linear SOI, the sample dependent characteristic fields for the phase coherence and the cubic SOI, respectively, and Ψ is the digamma function. Here the diffusion limit of this model is satisfied as the magnetic field we applied is much smaller than the B_e , the characteristic field of elastic scattering, which is on the order of 100 T because of the short mean free path in our heterostructures. In order to account for the classical Lorentz force which manifests itself as quadratic dependence in field, we fit the resistivity data directly using

$$R_{xx}(B) = \frac{\gamma}{(\Delta\sigma(B) - \Delta\sigma(0) + \delta)} + \alpha B^2 \quad (4.9)$$

where α is the coefficient for the Lorentz force, γ is the conversion factor and δ is the field independent component of conductivity. The data has been symmetrized to avoid any effect due to the choice of direction.

Figure 4.11 (a) Thickness dependent fitting parameters: B_{so1} and B_{so3} are characteristic fields of the linear and cubic SOI, respectively, and B_{ϕ} is the characteristic fields for the phase coherence. (b) The deduced spin relaxation lengths as a function of STO layer thickness in the heterostructures.

Figure 4.10 shows the result of fitting to the magnetoconductance data using the ILP model, and the derived fitting parameters are shown in **Fig. 4.11a**. Although the fitting has been done using the resistivity data, we present the conductivity results since it is a common practice in the literatures. As the main result of this work, the B_{so3} monotonously decreases from 3.75 T to 1 T as the thickness of the inserted STO increases from 8 uc to 60 uc, and the sample dependent B_{ϕ} fluctuates around 1-2 T, which is in line with the WAL mechanism. Besides, it is found that similar to the recent report by Nakamura *etc* [138], the SOI is dominated only by the cubic Rashba term at the heterostructure with STO thickness above 20 uc, while the linear Rashba

term $B_{\text{so}1}$ emerges at thinner well and also monotonously depends on the thickness of the STO. To further characterize the SOI in the heterostructures, the thickness dependence of spin relaxation lengths of linear and cubic SOI term are calculated via equation $l_{\text{so}} = \sqrt{\hbar/4eB_{\text{so}}}$. The length characterizes the strength of SOI, and its dependence on the STO layer thickness again confirms the effective tuning of the SOI (**Fig. 4.11b**).

4.5 Discussion and summary

The mechanism behind the tuning of SOI in our asymmetric heterostructures is different from the gating experiments recently reported for the oxide surfaces and interfaces [168]. No external gate bias is applied here, but a built-in electric field is expected to exist in our asymmetric oxide heterostructures as revealed in the XRD experiments (**Fig. 4.7b**). Such a built-in field is consistent with the electrostriction effect recently discovered at the LAO/STO interface [156]. Furthermore, the contraction of the out-of-plane lattice constant in STO is similar to the observation made on the electron-irradiated poly-(vinylidene fluoride-trifluoroethylene) copolymer with relaxor ferroelectric characteristics [169]. Considering the similar dependence on the thickness of the STO layer, we can infer a correlation between the built-in electric field in the STO layer and the tuning of spin-orbit interaction in the LAO/STO/LAO oxide heterostructures.

The thickness-dependent built-in electric field may not come from the charge transfer at the LAO/STO interfaces since the charge density from the polar

catastrophe should not depend on the thickness of the heterostructure. On the other hand, we should note that the strongly strained STO layer in these heterostructures may develop uniform ferroelectric polarization [37,170-171], which can also contribute to the built-in electric field and thus the SOI. In our LAO/STO/LAO asymmetric heterostructures, we expect a polarization $\mathbf{P}$ to be around 0.3 C/m^2 under the present strain condition [170], and consequently the polarization $\mathbf{P}$ leads to the existence of electric field $\mathbf{E}_0$ in the STO layer [172]. $\mathbf{E}_0$ can be roughly estimated as $\mathbf{P}/\epsilon$. In the strained STO layer, $\mathbf{E}_0$ can reach the order of MV/cm [37,170] and hence it is strong enough to exert significant influence on the SOI in the heterostructures [138]. Such electric dipoles along with hardened phonon modes were also reported in doped STO [173]. When the STO layer is thicker, the electric field may be spontaneously screened by the doped carriers [172], resulting into weaker SOI (**Fig. 4.11**). Recently, there have been a few proposals on the nonvolatile control of the Rashba spin-orbit coupling by integrating ferroelectric functionalities with the interface-based devices [174-175]. Our asymmetric oxide heterostructure offers an alternative structure-based route for manipulating SOI, and complements an earlier study [138] that suggests only cubic SOI is present.

Last, we want to mention the observation of the coexistence of linear and cubic Rashba effect. As so far, there are few reports discussing the scenario, we hope this may stimulate more studies on it theoretically and experimentally.

In summary, we demonstrate a new class of oxide heterostructures with asymmetric interfaces (LAO/STO vs. STO/LAO), and the SOI can be tuned by the

thickness of the STO layer while no external electric field is needed. All the carriers are confined in the heterostructures while their distribution is highly asymmetric with the interface carriers dominating the magnetotransport. Although STO has a centrosymmetric structure, the space inversion symmetry is broken in such heterostructures, and the built-in electric field in the STO layer leads to the tuning of SOI. We propose such asymmetric heterostructures as a new tool to explore the SOI and other exotic physics in oxide heterostructures.

Chapter 5

Conclusions and Perspectives

In this thesis work, I studied the transport properties of the LAO/STO heterointerfaces via the electric field effect (Chapter 3) and the strained asymmetric heterostructures (Chapter 4). In these experiments, I discussed the mechanism of the insulator-to-metal transition at the heterointerface, confirmed the existence of the Kondo effect at the high carrier density regime and its tunability by gate bias, and explored an alternative way to control the spin-orbit interaction at oxide heterointerfaces.

The Insulator-to-metal transition and Kondo effect were explored in the insulating 3 uc LAO/STO heterostructure through the electric field effect. In this work, we successfully applied the electric double layer transistor (EDLT) to the investigation of the oxide heterointerface, to achieve the electrostatic modulation. Through the carrier density dependence of conductance and magnetoresistance, we found that the electrostatically induced insulator-to-metal transition has the nature of inhomogeneous percolation transition. In the gate voltage range far away from the transition, a resistance upturn persists at the low temperatures, which was attributed to the Kondo effect with a magnetic origin. Furthermore, the Kondo effect was found to be tunable under the gate bias. Our results shed new light on the intriguing electronic and magnetic properties of the LAO/STO heterostructures and, in turn,

indicate that the heterostructure may offer another promising platform for the study of the important many-body effect.

Another interesting transport property of the oxide heterointerface is the spin-orbit interaction due to the broken inversion symmetry, which has been reported to be tuned directly or indirectly by the external electric field. In my thesis work, an alternative method to tune the SOI was explored on the LAO/STO/LAO asymmetric oxide heterostructure, in which only one n-type interface was present. Through reducing the thickness of the STO layer, we found that the strength of SOI at the oxide heterointerface was enhanced, demonstrated by the magnetotransport measurements. Furthermore, it was found that the SOI of the heterostructures with more than 20 uc STO was dominated by the cubic Rashba term, while it was codetermined by the linear and cubic Rashba term in thinner heterostructures. According to the Hall effect measurement and x-ray diffraction characterization, which indicated the presence of electrostrictive effect, we inferred that the SOI in the LAO/STO/LAO was dominated by the built-in electric field in the STO layer and, enhancing the thickness of STO resulted in smaller field and thus weaker SOI. Our results in this project offered a new method to control the SOI in artificial oxide heterostructures and also highlight the importance of the SOI in designing heterostructures to achieve the desired transport properties.

The transport properties explored in this thesis exemplify well the potential of the LAO/STO oxide heterointerface as a promising candidate for explorations of basic science and future oxide electronics. Definitely, there are still a lot of exotic

properties to be explored, as discussed in Chapter 1. The most puzzling issue should be the coexistence of the SC and FM in the LAO/STO heterostructure, which is one of the on-going research thrusts in this field. It also remains a tremendous challenge to find other high-performance interface systems besides the STO-based ones, and lots of research efforts are needed to improve the mobility of such 2D electron gas to match the level of conventional high-purity semiconductors, though the mobility above $10^5 \text{ cm}^2/\text{Vs}$ has been reported at $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$ heterostructure [176]. Both the field effect and the heterostructure approaches can be generalized to other interface-based materials and reveal the physics. More widely, if we look beyond the system of LAO/STO, the versatile properties of transition metal oxides and their interfaces offer us a larger and more exciting platform to explore not only the fundamental physics, but also their potential applications. We hope that in the near future such oxide interfaces can find their niche devices and applications complementary to the conventional semiconductor counterparts.

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