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Emergent Phenomena at the (111) LaAlO₃/SrTiO₃ Interface

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Samuel K. Davis

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ABSTRACT

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Samuel K. Davis

In his Nobel lecture Herbert Kroemer famously stated that "The interface is the device". While he made this statement in the context of semiconducting heterostructures, it has proven to be just as relevant for more complex materials, such as the transition metal oxides. In particular, the 2-D conducting gas that forms at the interface between two transition metal oxides $LaAlO_3$ and $SrTiO_3$ (LAO/STO) has shown that a system containing a rich phase space of phenomena can arise from the interface of two relatively boring insulators. These phenomena include superconductivity, magnetism, gate tuned metal to insulator and superconductor to insulator transitions as well as evidence of large spin-orbit coupling at the interface. While the observation of these effects has produced more than a decade of fervent research on the LAO/STO interface, these previous efforts have focused mainly on the (001) crystal orientation of the LAO/STO interface. This thesis presents the results of some of the first studies on the (111) orientation of the LAO/STO interface, which not only has a more complex interfacial symmetry, but also shows new emergent phenomena. The most striking of which is the observation of strong,

in-plane, anisotropy in the almost all of interface's electrical transport properties. The thesis will identify not only identify where this anisotropy "lives" in the (111) LAO/STO interface, but also examine the energy scale at which it onsets. These results are evidence of an electronic nematic state that breaks the rotational symmetry of the sample. Finally, it will explore how this anisotropy impacts the other phenomena present at the interface, superconductivity and ferromagnetism.

Acknowledgements

Very few graduate student careers are solitary endeavors and mine has been no exception. My work at Northwestern, least of all this document, would not have been possible without Professor Venkat Chandrasekhar. His patient guidance has steered my growth as a physicist, communicator, teacher, and leader. Under his tutelage, I not only learned to be a methodical experimentalist, but also the importance of being able to navigate the many other challenges that exist beyond the doors of the laboratory.

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¹Full disclosure: there were still explosions and even one fire, but such events were kept to a minimum.

While Varada Bal and one of the newer students, Aaveg Aggarwal, were denizens of the other office (not to be confused with the "cool" office), they were just as vital to my life as a graduate student. In particular, Varada has been an invaluable companion who was always willing to bounce ideas back and forth, or help me with whatever task was at hand.

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My sister Emily has always been there to listen to me celebrate my successes or vent about my failures. My parents Roxanne and Ted have and always will be the role models I strive to emulate. Their ceaseless love and support has served to anchor me even in my darkest hours.

Last, but certainly not least, Sheena you have been the best friend I have ever known, and you have certainly accrued a substantial number of billable hours over the last decade of our journey together. Don't worry, I know you will take my case pro bono.

Term	Abbreviations
Transition Metal Oxide	ТМО
LaAlO ₃	LAO
SrTiO ₃	STO
2 Dimensional Conducting Gas	2DCG
Electrostatic Backgate Voltage	V_g
Carrier Density	n
Carrier Mobility	μ
Longitudinal Resistance	R_L
Transverse Resistance	R_{XY}
Hall	R_H
Nematic Ordering Temperature	T_{nem}
Superconducting Transition Temperature	T_C
Superconducting Critical Current	I_C
Superconducting Critical Field Perpendicular to	$H_{C,\perp}$
the Sample Surface	
Superconducting Coherence Length	ξ_0
Freezing Temperature	V_F

List of abbreviations

Table 0.1. List of Abbreviations

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3.2 Argon ion etch parameters

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- B.1 Wisconsin Sample Numbers and Processing: The first column contains the sample chip numbers. The second column contains details on the post growth treatment conducted: none for the as-grown samples, oxygen annealed samples, UV irradiated samples, or Ar/H₂ annealed samples. Finally there is a column with notes on each sample. These notes describe the current state of the sample. 191

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B.2 Wisconsin Sample Numbers and Processing, Table 2: The first column contains the sample chip numbers. The second column contains details on the post growth treatment conducted: none for the as-grown samples, oxygen annealed samples, UV irradiated samples, or Ar/H_2 annealed samples. Finally there is a column with notes on each sample. These notes describe the current state of the sample. 192

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CHAPTER 1

Introduction

The broad field of condensed matter physics revolves around the search for and investigation of symmetry breaking in both bulk and nanoscale devices. Evidence of symmetry breaking is invaluable as it heralds new phases, such as superconductivity and ferromagnetism, which break gauge and time reversal symmetry respectively. These new phases of matter can be interesting not only from the stand point of fundamental physics, but also useful from the perspective of potential applications.

One class of materials that has served as a paradigm in the search for collective material states is the transition metal perovskite oxides (TMOs), shown schematically in Figure 1.1. In their simplest form perovskite materials have cubic symmetry and follow the formula ABO₃ where A is a rare earth or alkaline ion and B is a transition metal ion surrounded by an octahedral cage of oxygen. TMOs can exhibit a rich array of exotic phenomena, including those previously mentioned, which can be dramatically changed by swapping entirely different elements or more subtly via fractional doping. These effects and the subsequent tunability arise because electrons from the *s*-orbitals of the transition metal ions are transferred to the oxygen *p*-orbitals.^{1–3} This leaves only the strongly correlated *d*-electrons to govern electrical transport, magnetic response, optical response, superconductivity, and the interplay between any coexisting effects.¹

In addition to the rich physics found in the bulk, many TMOs have closely matched crystal lattice constants, allowing TMOs with drastically different properties to be grown



Figure 1.1. Ball and stick crystal unit cell of a simple ABO_3 transition metal perovskite oxide. The green sphere, labeled A, is an alkaline or rare earth ion; the blue spheres, labeled B, is a transition metal ion; and the red spheres, labeled O, are oxygen ions.

in heterostructures with atomic precision, one material on top of another.⁴ In this case, the close proximity of two disparate materials can lead to novel combinations of previously existing phenomena or even new effects unattainable in the bulk. Similar to the bulk phases, these phases are driven by symmetry breaking at the interface and their combinations are shown schematically in Figure 1.2.²

Arguably the most famous of such heterostructures is formed from the two band insulators $LaAlO_3$ (LAO) and $SrTiO_3$ (STO). In 2004, Ohtomo and Hwang found that



Figure 1.2. Diagram showing the most well known symmetries and degrees of freedom of strongly correlated electrons that can be manipulated at TMO interfaces. Figure from Ref. 2

when a critical thickness of LAO was grown epitaxially on (001) STO, a 2-dimensional conducting gas (2DCG) formed at the *n*-type TiO₂ terminated interface.³ The subsequent decade and a half saw an immense amount of research that explored the properties of the LAO/STO interface, finding that not only is the 2DCG truly confined to the interface, but that it also hosts a superconducting state,^{5–7} magnetism,^{8–13} gate tunable metal/superconductor to insulator transitions,^{14,15} and strong spin orbit coupling.^{16,18,19}

Additionally, the LAO/STO interface is one of the few known systems to support the coexistence of superconductivity and magnetism, which are traditionally thought to be antagonistic.^{20–23} The interaction between these two phases gives rise to the manifestation of charge vortex duality at the interface.²³ For the most part however, the study of these effects has been confined exclusively to the (001) orientation of the LAO/STO heterostructures.

Recently it has been shown that, in addition to the (001) orientation, both the (110) and (111) orientations of the LAO/STO heterostructures play host to their own 2DCGs.^{24,25} The (111) orientation is of particular interest as it has hexagonal symmetry similar to graphene, the transition metal dichalcogenides, and many topological insulators.^{26–28} In this thesis, I will present my work in characterizing the (111) LAO/STO interface using low temperature electrical transport measurements, showing that, like the (001) orientation, the (111) LAO/STO interface supports the coexistence of superconductivity and magnetism.^{29,30} I also that found the (111) LAO/STO interface shows clear evidence of hole like transport,^{31,32} a low temperature memory effect that onsets only at mK temperatures,³⁰ and suprisingly the existence of strong anisotropy between mutually orthogonal in-plane crystal directions.^{29–32} This anisotropy is tunable via an electrostatic backgate voltage and post growth treatment, survives into the superconducting state, and is an important signature of rotational symmetry breaking at the interface. Such symmetry breaking may lead to an electronic nematic phase similar to the ones seen in the iron based superconductors,³⁴⁻³⁶ Half integer quantum hall states,³⁷ and some topological superconductors.38

In what follows I will outline the organization of the remaining chapters in this thesis.

Chapter 2 will detail the theoretical background as well as previous experimental results. I will briefly discuss the band structure and electronic characteristics of bare STO before moving into a deeper discussion of the structural transitions that have been observed. These structural transitions proved to be an integral part of the story that surrounds the anisotropy I observed in the (111) LAO/STO heterostructures. I will then highlight some of the properties of the (001) LAO/STO heterostructures, focusing on formation of the 2DCG, the role of oxygen vacancies at the interface, the coexistence of superconductivity and ferromagnetism, evidence of strong spin-orbit coupling at the interface, and most importantly, sources of anisotropy at the interface. In the last section of this chapter, I will discuss the (111) LAO/STO orientation of the interface, concentrating on the structural differences and how they lead to a more complex symmetry in the Fermi surface. Finally, I will discuss the experimental results that have been reported thus far on conduction in (111) LAO/STO and (111) STO interfaces.

Chapter 3 will focus on the experimental techniques used to investigate the (111) LAO/STO samples. I will start by reviewing the sample patterning and etching process, which uses UV photo-lithography and Ar ion milling to define the Hall bar devices used in my research. I will also discuss the AFM, photo luminescence, and X-ray characterization of my samples, which allow me determine the surface, chemical doping, and crystalline properties of the samples. Finally, I will describe the electrical transport techniques used

to measure these devices, which due to the large resistivity of the (111) LAO/STO interfaces, present unique measurement challenges that must be carefully addressed. Included in this last section I will describe the technique I helped develop to measure the quantum capacitance of the 2DCG and describe how it is a measure of the density of states.

Chapter 4 presents the meat of the thesis, containing my experimental data and subsequent analysis, and is divided into two main sections. The first section deals with data taken at $T \ge 4.0$ K and is broken up into subsections detailing the evidence of anisotropy, tuning the anisotropy with post growth treatment, and evidence for an electronic nematic state at the interface. The second section considers data taken at $T \le 4$ K and is also broken into three subsections on superconductivity, magnetoresistance, and the memory effects that I observed at ultra low temperatures. In each of these subsections I will not only present the data and analysis for each measurement, but also discuss how these results compare the (001) LAO/STO heterostructures and other similar systems.

Finally, in Chapter 5 I will conclude the thesis by summarizing my findings as well as discuss future avenues for research. These include milli-Kelvin scanning probe measurements, high-field magnetoresistance measurements, and measurements on ionic gel gated (111) STO which will help to pin down the origin of anisotropy in the system.

CHAPTER 2

Background and Previous Work

In this chapter, I will review the theoretical and experimental background necessary for understanding effects observed at the LAO/STO interface, as well as the motivation for moving beyond the (001) orientation of the LAO/STO interface. This chapter is divided into 3 major sections. In the first section, I will discuss the electronic and structural properties of STO.^{47–49} STO is not only used ubiquitously as a substrate for other perovskite materials (such as superconducting YBa₂Cu₃O_{7–x}, ferroelectric BaTiO₃, La_{1-x}Sr_xMnO₃, etc),^{56,57} but it also exhibits many fascinating properties on its own.^{42–44,46,58,59} I will then review how surface states can nucleate on the bare surface STO and how these surface states relate to the buried 2DCG at the LAO/STO interface.^{60–62,64} In the last portion of this first section, I will describe the structural transitions that occur in STO.^{41,65–67,70,71,73,74}

The second section of the chapter will examine the (001) LAO/STO interface, starting with the origins of the 2DCG,^{11,82–86} with a particular focus on the role of oxygen vacancies at the interface.^{8,89–91,93} I will then describe the many effects seen at the interface.^{14–16,18–23} Finally, I will end the second section by reviewing signatures of anisotropy at the (001) LAO/STO interface.^{105,106}

The last section of this chapter will be devoted to examining the structural differences between the (111) and (001) LAO/STO interfaces and the consequences for the symmetries present in the Fermi surface.^{26,27,109–113} I will start by giving an overview of the experimental results in the growth and tuning of the conductivity at the interface. I will also review the predictions that stem from these more complex symmetries, including the predictions of topological insulating behavior,²⁸ nematic behavior,¹⁰⁷ and unconventional superconductivity.¹⁰⁸

2.1. Electronic and Structural Properties of SrTiO₃

2.1.1. Band Structure

In its bulk form, and at room temperature, STO is a band insulator with a band gap of 3.3-3.5 eV,⁴ with a cubic perovskite crystal structure (space group Pm3m),⁴ lattice constant of 3.905 Å,⁴ and a relatively large room temperature dielectric constant of 300.^{41,65} While at first STO appears to be a relatively uninteresting band insulator, it has been found to host a wide variety of effects, leading Nobel laureate Karl Muller to dub it the "drosophila" of solid state physics.⁴¹ As I will show in later sections, it is actually the bands of the STO itself that lead to many of the effects seen at the LAO/STO interface. In fact, the 2DCG that forms in LAO/STO heterostructures has been found to live in the first few atomic layers of the STO and nearly all of the properties that have been observed at the LAO/STO interfaces have been observed in bare STO. Thus it is crucial that we understand the electronic structure of the STO itself.

From a historical perspective, theoretical studies in STO were motivated primarily by the observation of semiconducting behavior in doped STO samples.^{42–44,46} The initial semiconducting properties were found by annealing the STO samples in a reducing atmosphere, causing the samples to change in color as well as become conducting due to the formation of oxygen vacancies in the STO,⁴⁶ which act as electron donors causing it to become semiconducting.^{44,48} Other elements could be doped into the STO. Nb doped STO samples were particularly interesting as they were found to be superconducting at temperatures of a few hundred milli-Kelvin.^{42,43,46} Experiments also revealed that even in non-superconducting STO samples, the conductivity and mobilities increased dramatically at low temperatures, to $10^4 \ (\Omega \text{cm})^{-1}$ and $10^3 \ \text{cm}^2/\text{Vs}$ respectively,⁴⁸ pointing to a conduction band picture rather than a hopping scenario. This fostered a number of theoretical efforts centered on calculating band structure and elucidating the observed effects.^{47–49}



Figure 2.1. **STO Unit Cell**: A ball and stick model of the cubic Ti centered $SrTiO_3$ crystal unit cell. The lattice constant a_0 is 3.905 Å.² The green spheres represent Sr atoms, the teal sphere represents Ti, and the red spheres are oxygen ions.

For any material, the starting point for a band structure calculation is the crystal unit cell. Figure 2.1 shows a diagram of the stoichiometric STO unit cell where each Sr ion has a valency of +2, the Ti ions have valency of +4, and the oxygens have a valency of -2. In many cases the ionic approximation was found to be sufficient to describe the gualitative nature of the STO band structure.^{1-3,47} This approximation starts with the electrons in free ionic states shifted by the electric potential energy on each site. The tight binding approximation was then used to calculate the band structure based on the crystal symmetry present.⁴⁷ Kahn and Leyendecker (K-L) used this method on cubic STO and found that the band gap was formed between the filled O 2p bands and the Ti 3d orbitals.⁴⁷ Furthermore, K-L found that these two sets of bands were the primary homes for any electronic phenomena in the STO system. The next closest conduction (valence) bands were the Ti 4s / Sr 5s, (O 2s), and were 10 eV above (below) the Ti 3d, (O 2p) bands.⁴⁷ However, as shown Figure 2.2, the predicted energy band gap at the Γ point was discovered to be highly sensitive to the oxygen ionicity. For calculations done at the full O^{-2} valence the band gap was nearly 15 eV, far higher than the experimentally observed band gap of 3.3-3.5 eV. In fact, it was only at an oxygen valency of \approx -1.7 e that the experimental band gap is recovered, which implied that orbital overlap plays a not insignificant role in the physics at the interface.⁴⁷

In order to rectify this discrepancy, Mattheiss used the augmented-plane-wave (APW) method coupled with the tight binding model to calculate the band structure of STO.⁴⁸ He observed that, similar to K-L, the band gap forms between the O 2p and Ti 3d bands. The Ti 3d bands were then further split into the t_{2g} (comprised of the d_{xy} , d_{xz} , and d_{yz} orbitals) and the e_g bands (comprised of the $d_{x^2-y^2}$ and d_{z^2} orbitals) by the crystal field



Figure 2.2. **Ionic Approximation**: Band energies as a function of oxygen valency for STO orbitals. To calculate these bands the ionic approximation was used in conjunction with the tight binding model. The dashed line indicates the oxygen valency required to recover the experimental band gap. Figure and caption adapted from Ref. 47.

of the cubic lattice.⁴⁸ Mattheiss's results, represented in Figure 2.3(a), showed that the splitting was approximately 2 eV, where the t_{2g} was the lower energy of the two sets, and they further found that near the conduction band minima, at the Γ -point, the dispersion was parabolic. This dispersion implied that electrons in these bands could be considered free and their mass was determined by the band curvature. While all three bands were found to be degenerate at the Γ -point, moving along the < 001 > family of directions ($\Gamma \rightarrow X$) lifted the degeneracy so that the in-plane bands had a larger mass. For example, along the [001] direction, and perpendicular to the (001)-plane, the d_{xy} bands had larger mass in the [001] direction than the $d_{xz,yz}$ bands and, thus, a shallower dispersion (see Figure 2.3 (b)).⁴⁸



Figure 2.3. (a) Full APW+tight binding calculations for the cubic (001) STO Brillouin zone.⁴⁸ I have highlighted the conduction and valence bands formed by the titanium t_{2g} oxygen 2p bands respectively. Also included is a diagram of the Brillouin zone with the directions used in the calculation. (b)Band diagram for the titanium t_{2g} bands showing that, while degenerate at the Γ -point the different t_{2g} orbitals have different mass along in-plane direction. In this case along the in-plane k_y direction the d_{xz} band has a larger mass, weaker dispersion, than the $d_{yz,xy}$. (c) DOS averaged over the Brillouin zone, again the valence bands and conduction bands are highlighted. Figure and caption adapted from Refs. 48 and 61.

Figure 2.3(c) shows Mattheiss's calculated density of states (DOS) for STO, where the the band gap was found to be $\approx .25 \text{ Ry} = 3.4 \text{ eV}$, in good agreement with experimental observations. However, these calculations neglect a few important experimentally observed interactions. First, these calculations were conducted by imposing Kramer's (spin)

degeneracy, which in stoichiometric STO is a fairly good assumption as the Ti⁺⁴ ions have an electron configuration of $[Ar3d^04s^0]$, leaving no unpaired d-shell electrons, and thus no magnetic moment. However, the addition of dopants/defects has been shown to reduce the Ti⁺⁴ to Ti⁺³, which has an electron configuration $[Ar3d^14s^0]$ and exhibits a magnetic moment due its unpaired d-shell electron. Thus, Mattheiss's calculations may have missed many of the magnetic effects that have been observed in LAO/STO systems.^{8–13} Second, the calculations did not include spin-orbit interactions, which have been shown to be extremely large (possibly on the order of 100 meV) in STO and LAO/STO.^{16,18,19,62} These interactions are expected to further lift the degeneracy of the t_{2g} conduction bands via spin splitting. Finally, the calculations did not address the evidence of surface states in the system. Evidence for these states existed as early as 1965 when Cardona and Kurtz observed a difference in reflectivity measurements based on surface preparation.^{50,51} These surfaces states have proven to be vital to understanding the physics at the LAO/STO interface and are thus the subject of the next section. In fact, in many ways they are identical to the 2DCG that forms at the LAO/STO interface.

2.1.2. Electronic Surface States

While hints of surface states were first observed by Cardona and Kurtz,^{50,51} it wasn't until 2011 that they began to be fully explored, when Santander-Syro *et al.*⁶¹ found that they could observe high intensity photo-emission from the surface of STO substrates cleaved in vacuum. In order to explain these findings Santander-Syro *et al.* proposed that a confining potential existed at the STO surface and was created by a homogeneous positive charge density that generated an electric field, F, inside the STO.⁶¹ The confining potential

took the form $V(z) = -V_0 + eFz$, and acted to lower the energy of the Ti 3d bands at the Γ -point, this potential is depicted schematically in Figure 2.4(a). This confinement potential resulted in a splitting of the bands that was inversely proportional to their masses. These bands, shown in Figure 2.4(a), are quantized, labeled $E_n(d_{i,j}), n = 1, 2, ...,$ and the d_{xy} band had the highest mass and thus the lowest energy.⁶¹ On the other hand, the $d_{xz/yz}$ were significantly split from and higher in energy than the d_{xy} bands; however, they were still degenerate at the Γ -point. This degeneracy could be further lifted via a variety of mechanisms such as spin-orbit coupling and structural transitions which would lead to further splitting of the bands, as shown in Figure 2.4(b).⁶¹ It is important to note that the schematics in Figure 2.4(a) & (b) were plotted as a function of k_y ; therefore, d_{xy} , although heavy along the z direction, had a strong dispersion in the plot. Other mechanisms could lead to surface states states at the interface. One example are the so called Schockley-Tamm surface states which arise due to the mismatch in crystal potential experienced by electrons at the interface between the bulk crystal and vacuum.^{52,53} These states have sub-band gap energies and wave functions that decay exponentially as a function of depth into the crystal, 52-54 and could be used to describe the surface states in SrTiO₃.⁵⁵ However, Santander-Syro *et al.* attributed their confining potential solely to a homogeneous layer of positive charge at the interface formed by oxvgen vacancies.⁶¹ Furthermore, on undoped, uncleaved, substrates there were no sign of the surfaces states, leading to the conclusion that the surface states were extrinsic in nature, limiting the possibility that Schockley-Tamm States were the origin of theese surface states.

The photo-emission, measured by high resolution ARPES, showed that around the Γ point there were multiple strongly dispersing and weakly dispersing bands. Figure 2.4(c) takes a close look at the band structure by combining the vertically and horizontally polarized response of the ARPES measurements such that five different bands become clearly visible and are marked with dashed red, blue, and green lines. Two strongly dispersing bands (i.e. light mass carriers) exist and were separated by ≈ 100 meV, where the upper (lower) band labeled with dashed red (blue) had a band edge at 100 (210) meV below the Fermi energy. Both bands had an effective electron mass of $m^* \approx 0.7m_e$. They also found that the two weakly dispersing bands (i.e. heavy mass carriers) existed at the interface with $m^* \approx 10m_e$. The most interesting observation by Santander-Syro *et al.* was that there was no sign of degeneracy anywhere about the Γ -point; thus, implying that there strong spin-orbit interactions may exist at the interface.⁶¹ Finally, by mapping the ARPES response as a function of k_x and k_y and then integrating the intensity over the entire Fermi surface they found the carrier density was $n \approx 10^{13}$ cm⁻².⁶¹

Spin-orbit coupling at the interface is of particular interest due to the recent observation, again by Santander-Syro *et al.*, of spin split bands at the STO surface. Spin-orbit coupling at the surface can arise when the large electric field associated with a confining potential interacts with magnetic moments present at the interface.⁶² In these measurements the samples were prepared by cleaving atomically flat, TiO₂ terminated, (001) STO in vacuum, which drastically increased the signal to noise ratio in the ARPES experiments.⁶² As shown in Figure 2.5(a), an opposite k_y -shift occurred in the intensity maxima when the polarity of the excitation light (either right or left circularly polarized) was changed. Measuring this intensity shift as a function of energy (Figure 2.5(b))



Figure 2.4. Band Structure of the STO of Surface States: (a)Sideby-side representation of the LV and LH spectra around Γ_{102} for the nondoped sample. The dotted lines are tight-binding representations of the bands, following the same colour scheme as in (b) & (c). (b)Quantum well states, or subbands, resulting from the confinement of electrons near the surface of SrTiO3. The inset shows a wedge-like potential created by an electric field of strength F at the surface, which we use as a simple model to analyse the ARPES data . (c), Additional degeneracy lifts at Γ occur as a result of spin-orbit coupling, tetragonal and orthogonal distortions, or possible surface reconstructions. This subband hierarchy is the one that best represents the experimental results. Figure and caption adapted from Ref 61

showed that not only were there spin split bands in k_y , but there also existed a gap at the Γ -point, yielding two nested, helically textured, bands split by 100 meV in k_z . Unfortunately, identical measurements conducted by McKeown-Walker *et al.*⁶³ did not observe this splitting. Thus the precise nature of this splitting is still in question. Nevertheless, such a spin splitting, if it exists, in an electrically conductive material would lock the



Figure 2.5. Spin Split Bands at the STO Surface: (a) Intensity response of (001) STO as a function of k_y and circular polarization. (b) Full energy scan with I_Q^{Down} . The bracketed section corresponds to the blue trace in (a). Note the lower intensity for $k_y > 0$ Å⁻¹. (c) Schematic diagram of the gaped helically spin polarized bands observed at the (001) interface. The gap between the upper and lower bands is ≈ 100 meV, four times higher than room temperature. Figure and caption adapted from 62.

charge carrier spins to their momentum, opening up a new avenue for spin polarized electronics. More intriguingly, when combined with the superconductivity that also occurs at the interface/surface this spin texture is one of two of the main ingredients necessary for the existence of the rabidly sought after Majorana fermion.²⁸

2.1.3. Structural Transitions

Much of the analysis of STO's band structure and surface states in the previous subsections relied on the assumption that STO had cubic crystal symmetry. It is this symmetry that splits the t_{2g} and e_g orbitals and determines the directional dependence of the light and heavy carrier bands.^{47,48,61} However, the analysis swept under the rug the multitude of observed and predicted structural transitions, which lower the symmetry of the STO system. In this section, I will examine the historical evidence of such structural transitions, discuss the implications for the band structure and electronic properties of STO, and finally discuss the interesting quantum paraelectric transition that arises from these structural transitions.



Figure 2.6. STO: Tetragonal Crystal Structure: (a) Schematic of the oxygen octahedral rotation that occurs during the cubic to tetrahedral transition that occurs at T=105 K (b) Brillouin zone for the tetragonal unit cell showing the *k*-space directions. Figures and caption adapted from Ref. 49

Stoichiometric STO has been experimentally observed in two well studied phases: cubic and tetragonal.^{41,65–67,70,71} A few studies have found a small amount of evidence lower symmetries such as orthorhombic and rhombohedral phases;^{73,74} however, determination of these lower symmetry phases has been complicated due to the formation of small disordered domains and the extremely small distortions of the lattice ≈ 0.6 mÅ.^{72,106} On the other hand, the tetragonal phase has been extremely well characterized and is driven by a second order transition that occurs at $105 \sim 110$ K, as observed via xray crystallography,⁶⁸ ultra-sound experiments,^{44,45} and dielectric response,.^{41,65,71} The previous experimental studies have found that the *c*-axis does not expand by any significant amount,;^{48,49,68} in fact at T = 77 K, $c = 1.0006 * a.^{68,69}$ Instead, as is shown in Figure 2.6, the oxygen octahedra were found to rotate about the titanium atoms such that neighboring octahedra rotated counter to each.^{68,69}

In order to study the effect of this transition on the electronic band structure of STO, Mattheiss and others performed APW-Tight binding calculations on the tetragonal structure under the assumption that the rotation of the oxygen octahedra was perfectly rigid,,⁴⁹ i.e. no distortion of the Ti or Sr atoms, which agreed with the observed experimental distortions.^{68,69} They also omitted any contribution of the bands other than the O 2p and Ti t_{2g} . Mattheiss's results are presented in Figure 2.7 for the cubic unit cell as well as two tetragonal unit cells with 0°, 1°, and 2.1° of octahedral rotation: for reference the Brillouin zone is shown in Figure 2.6 (b).⁴⁹ The clearest change in band structure occurred along the Δ direction, which in real space corresponded to the [001] direction. For non zero rotations, Mattheiss observed a splitting at the Γ -point between the d_{xy} and $d_{xz,yz}$ bands on the order of 30 meV, similar to the splittings observed in the STO surface states. Other directions in the Brillouin zone also showed lifting of the degeneracy at the Γ -point, most notably along the Σ direction, corresponding to the [110] direction.

It is important to note that although these calculations were done with the simplifications described, later calculations with fewer assumptions and more accurate basis sets confirmed the magnitude and nature of these effects. The greatest oversight of these calculations was that they were performed assuming single crystal samples.⁴⁹ In reality



Figure 2.7. STO: Tetragonal Band Structure: Full APW+Tight binding calculations for the cubic and tetragonal (001) STO Brillouin zones for three tetragonal rotations $\phi = 0$, 1°, and 2.1°. Figure and caption adapted from Ref. 49.

it was found that the cubic to tetragonal structural transition in the STO crystal occured via the nucleation of microscopic domains as seen in optical micrograph in Figure 2.8(a) as well as in the low temperature SEM image of an LAO/STO heterostructure in Figure


Figure 2.8. STO and LAO/STO: Tetragonal Domains: (a) Photomicrograph of (001) STO crystal at 85 K from Ref. 72. (b) LTSEM map for different samples showing different patterns of twin walls on (001) LAO/STO from Ref. 76. (c) Map of the lateral electromechanical response, at $V_q = -27$ V. The bulk of the image is colored white, indicating negligible lateral electromechanical response, whereas the upper half of the image contains a network of paired red and blue stripes elongated in both the x- and y-directions. The stripes are peaks of alternate response, each representing the motion of either the rising (red) or falling (blue) edge of a potential step at the surface. (d) Tiling rules of tetragonal domains in STO: the three possible domains are labeled X, Y, and Z according to the orientation of their long axis (a axis). (e) To minimize dislocations, intersections of tetragonal domains of different orientations must share their short axis (a axis), forming twin boundaries with well-defined angles. (d) A schematic map labeling the domain orientations in (c) The red and blue stripes are the domain wall boundaries. The coloring of the domains follows from the tiling rules in (d). Figures (c)-(f) and captions adapted from Ref. 75.

2.8(b).^{72,75,76,106} These domains each had an extended c-axis along one of the < 001 > family of directions (Figure 2.8(d) & (e)) and were separated by ferroelastic twin walls, which had been observed by a wide variety experimental techniques, but most strikingly



Figure 2.9. Dielectric constant, ϵ , as a function of temperature for STO along the [110] direction. Inset $1/\epsilon$ vs T showing the fit to classical mean field theory; a distinct deviation from mean field occures at ≈ 36 K. Figure and caption taken from Ref. 65.

via scanning single electron transistor imaging on LAO/STO samples, as shown in Figure 2.8 (c).^{75,76,106} In unstrained STO with a low miscut angle these domain walls occured randomly, as show in Figure 2.8(a),(b), & (c), and had length scales that ranged from 100 nm to 100s of μ ms.^{75,76,106} Furthermore, it was found that these domains formed completely randomly. Upon cycling through the structural transition temperature; in most experiments with stoichiometric STO samples, there were no signs of persistent memory effects.^{72,75,106}

A final consequence of the cubic to tetragonal structural transition was detected by Muller *et al.*,^{41,65} who found the dielectric constant starts to sharply rise at T = 37 K and saturated at T = 4 K after attaining a value of 22000.⁶⁵ This rise in ϵ was attributed to the increase soft phonon mode frequencies which occurred at low temperatures, and was subsequently dubbed a quantum anti-ferrodistortive transition,^{41,65,70,71} because the zero-point motion of the octahedra resisted the transition to a ferroelectric state. This extremely high dielectric constant has made electric gating of the STO and LAO/STO devices very effective at changing various sample properties . It should be noted that the ϵ dropped to < 1000 for fields greater than $E \approx 2 \text{ MV/m}$;^{41,65,67,71} however, this Efield strength corresponds to an electrical potential ~ 1000 V on most STO commercially available substrates, far greater than any field applied in this work.

2.2. The (001) LaAlO₃/SrTiO₃ Interface

In this section, I will discuss the origins and effects seen in the 2DCG at the (001) LAO/STO interface, starting with a brief historical account of the discovery of the LAO/STO 2DCG and the mechanisms by which it forms. While there are two main mechanisms, I will focus primarily on the role of oxygen vacancies at the interface, as the polar catastrophe has been covered in great detail by previous students. Furthermore, in later sections, we will see that for the (111) interfaces studied in this thesis, the role of the polar catastrophe may be strongly muted or must be treated on the same footing as oxygen vacancies in the system. I will then give a brief overview of the effects seen in the (001) LAO/STO interfaces; again these topics have been covered at great length previously, so I will only provide highlights of the findings. Finally, I will detail the reports of anisotropy at the (001) interface and their sources, as these reports will provide a critical contrast with my measurements on the (111) LAO/STO interface.

2.2.1. Origins of the 2DCG

The early 2000's saw a large influx of work towards the realization of transition metal oxide heterostructures with polar discontinuities due to the possibility of nontrivial structural and electronic structure.^{1-3,58,79} While the early work focused on superconducting copper oxides, ferroelectric heterostructures and manganite tunnel junctions, Ohtomo and Hwang showed in 2004³ that by growing two insulating perovskite oxides on top of each other they could, for the correct growth conditions, produce a conducting interface. These insulators were of course LaAlO₃ (LAO) and SrTiO₃ (STO) and have since been used as a new model interface for realizing exotic physical phenomena. As a reminder, LAO and STO are both layered insulating perovskites consisting of alternating AO and BO₂ layers with band gaps of 5.6eV and 3.5eV, respectively.² In the (001) direction the LAO is polar and alternates in charged layers of (LaO)⁺¹ and (AlO₂)⁻¹, while the STO is non-polar and alternates in charge neutral layers of (SrO) and (TiO₂).

In their original paper Ohtomo and Hwang found that by growing LAO epitaxially on atomically flat, singly terminated, (001) STO subtrates they could observe the nucleation of a conducting gas at the interface, provided more than 4 unit cells (UCs) of LAO were grown, as shown schematically in Figure 2.10(a).³ The singly terminated STO, either TiO₂ or SrO, was achieved by either etching the sample with hydrofluoric acid and then annealing it to achieve the TiO₂ terminated interface, or by growing a single layer of SrO via pulsed laser deposition (PLD) before growing the subsequent LAO layers.^{2,3} As the layers are constrained to alternate AO/BO₂, the two possible interfaces were $(AlO_2)^{-1}$ grown on SrO or $(LaO)^{+1}$ grown on TiO₂, as shown in Figure 2.10(c) and (d).^{2,3,24,77} Based on the ionic model from the previous chapter, the former interface was identified



Figure 2.10. Conduction at the (001) LAO/STO Interface: (a) 2DCG sheet conductivity vs LAO over layer thickness. (b) Resistance vs Temperature for both the P-type/N-type interface, schematically shown in (c)/(d). Figure 2.10(a) is adapted from Ref. 5, Figure 2.10(b) is adapted from Ref. 77, and Figure 2.10(c) is adapted from Ref. 3.

as a p-type interface and the latter as a n-type interface, where half a hole/(electron) was present at the interface per surface unit cell.^{?,1,24,47,77} However, as can be seen in Figure 2.10 (b) only the n-type (TiO₂/LaO) interface was found to be conducting. The SrO/LaO₂ interface on the other hand was fairly insulating at room temperature, became more conductive at temperatures 70 K $\leq T \leq 150$ K, below which the interface became highly insulating, R >> $10^7 \Omega$.^{24,77}

2.2.1.1. The Polar Catastrophe

The first proposed mechanism to explain the formation of the 2DCG at the interface was the so called polar catastrophe, which arises from the fact that polar LAO contacts nonpolar STO.^{11,82,83,85-87} As can be seen in Figure 2.11,⁸⁷ this results in a discontinuity in the electric potential at the interface that diverges as additional charged layers of LAO are added. As neither our LAO/STO samples, nor or any other stable, layered, polar material exhibit spontaneous electric breakdown, there must be some sort of reconstruction that compensates the potential build up.^{24,77,87} In the case of polar insulator/vacuum interfaces this compensation comes from physical surface reconstruction, where the stoichiometry of the surface changes to remove the surface charge.^{24,77,87} However, at the interface between LAO and STO an electronic reconstruction is predicted to occur instead of a physical one, canceling out the diverging electric potential by transferring half a charge carrier per surface unit cell to the interface, as shown in Figure 2.11.

These electrons transfer into the Ti t_{2g} bands in the STO layers at the interface, changing half of the Ti⁺⁴ to Ti⁺³ per surface unit cell.^{2,77,87} This reconstruction results in a 2DCG with theoretical carrier density $n \approx 10^{14}/\text{cm}^2$,^{2,77,87} similar to the previously discussed 2DCG that was induced at the bare STO surface by vacuum exfoliation.⁶¹ A similar process does not occur in the *p*-type, SrO terminated interface, as it is far more difficult to achieve the Ti⁺⁵ state; thus, no mobile holes are created, resulting in an insulating interface. An intuitive way of thinking about the interface is to consider it in the framework of semiconducting heterostructures. In the most basic p/n-junction, transfer of mobile charges from one material to the other creates a depletion region surrounding the interface and the space charges. These space charges cause band bending at the



Figure 2.11. Schematic representation of the polar catastrophe mechanism, where the left portion corresponds to the heterostructure pre-electronic reconstruction and the right corresponds to the reconfigured heterostructure. Adapted from Ref. 87.

interface between the p and n type materials. Analogous band bending occurs in the LAO/STO interfaces, where the "space charge" in the system is created by the polar LAO layers.^{77,88} In the case of the n-type interface, the positively charged (LaO)⁺¹ layer results in an electric field at the interface that extends into the STO. This electric field creates an electric potential that bends the bands in the STO downwards (i.e. lowers the energy of the bands) in a manner similar to the schematic potential shown in Figure 2.4(b). When the conduction band edge of the STO lowers below the chemical potential for electrons in the system, it will fill with mobile electrons. The potential generally extends into the STO about ≈ 0.8 to 20 nm for the (001) LAO/STO interface and has a strength of 0.2 to 0.3 eV; however, both figures are strongly dependent on other variables, such as oxygen vacancy concentration.

The major triumph of the polar catastrophe model is that it correctly predicts the thickness dependence of the 2DCG, i.e. for crystalline heterostructures with only a few monolayers of LAO there is no electronic reconstruction.^{2,77,79,87} However, the polar catastrophe fails to elucidate a number of questions: why the densities observed in most LAO/STO heterostructures are far lower than the density of $n \approx 3 \times 10^{14}$ /cm² predicted by the theoretical studies of the model;^{3,5-10,13,20} why the carrier density does not continue to grow with increasing LAO thickness;^{2,24,77,87} or why 2DCGs exist at interfaces that do not exhibit polar discontinuities.²⁴ These discrepancies imply that there are other mechanisms for conduction. Prime among these alternative roads to conduction are oxygen vacancies at the interface, the topic of the next section.

2.2.1.2. Oxygen at the Interface, or Lack Thereof

As I discussed in previous sections, oxygen vacancies have been historically utilized as electron dopants in bulk STO and,^{43,44,93} more recently, to induce the surface states observed via ARPES on bare STO.^{60–62,64} In both the bulk and bare STO cases, the oxygen vacancies donate 2 electrons to the interface per vacancy. These electrons transfer into the Ti t_{2g} bands changing the Ti⁺⁴ to Ti⁺³.^{2,77–79,87} Oxygen vacancies have the same effect in the LAO/STO heterostructures and can be introduced during growth,^{89–92} post-growth annealing, bombardment by energetic ions, UV irradiation in vacuum, etc, and can change the electronic properties of the interface. In particular, interface growth in different oxygen partial pressures dramatically changes the concentration of vacancies at the interface.^{8,77} Figure 2.12 shows that when the heterostructures are grown in very low oxygen partial pressures the sheet resistance is low, on the order of 10 mΩ.⁸ This low resistance is expected when the number of oxygen vacancies is large and Brinkman et al.'s⁸ samples also exhibit metallic behavior as a function of temperature. Brinkman et al. also found that when LAO/STO heterostructures are grown in high oxygen partial pressures (thus the samples have few oxygen vacancies), the resistance is 7 orders of magnitude higher and weakly insulating in nature; shown most clearly by the increasing, but saturating resistance in Figure 2.12.⁸ However, as a number of studies have pointed out, oxygen vacancies change more than just the resistivity of the 2DCG. They also have a hand in determining if it exhibits magnetic behavior, superconducting behavior, etc. This is shown schematically in Figure 2.12.^{2,8,77-79,87}

In order to further investigate the role of oxygen vacancies, Liu *et al.*⁸⁹ grew (001) LAO/STO interfaces not with crystalline LAO but with amorphous LAO (aLAO) deposited on atomically flat STO with a mixed termination. Because there was no well defined TiO₂/LaO interface, the role of the polar catastrophe was greatly reduced. Liu *et al.* and others found that even in these amorphous heterostructures, a 2DCG can be formed by finely tuning the growth conditions. This has many of the same characteristics as the one formed at the crystalline interface.^{24,89} Figure 2.13 shows the results measured by Liu *et al.* for amorphous heterostructures formed from 20 nm of aLAO grown on (001) STO at 750° C in various oxygen partial pressures.⁸⁹

Figure 2.13(a) shows Liu *et al.* found that the sheet resistance for the various samples differed at temperatures greater than ≈ 100 K, but converged below that.⁸⁹ Liu *et al.* found similar differences by measuring the temperature dependence of the carrier density, n, as shown on the left axis of Figure 2.13(b) where differences existed in the samples above 100 K. However, the mobilities, μ , remained roughly the same over the entire



Figure 2.12. Effects of Changing Oxygen Vacancies: Sheet resistance vs temperature for (001) LAO/STO heterostructures grown in different oxygen partial pressures. These different growth pressures create different concentrations of oxygen vacancies which not only change the resistance of the interface, but also give rise to different effects such as superconductivity and ferromagnetism. Figure adapted from Ref. 8.

 $4 \leq T \leq 300$ K temperature range. Taking a closer look at these results showed that samples grown in higher partial pressures of oxygen had higher resistance and a lower n at high temperatures, in good agreement with there being fewer oxygen vacancies at the interface. Conversely, samples grown in low oxygen partial pressures exhibited low resistance and higher n, pointing to a larger concentration of oxygen vacancies.⁸⁹

Further evidence that this behavior is due solely to oxygen vacancies comes from Figure 2.13(c) which shows that the samples become insulating for all 5 sample growth



Figure 2.13. Temperature Dependence of Oxygen Vacancy Carriers: (a) Sheet resistance vs temperature for 20 nm of aLAO grown on randomly terminated (001) STO. Each trace is for a LAO/STO heterostructure grown in different oxygen partial pressures. (b) Carrier density n and mobility μ as a function of temperature for the same heterostructures as in (a). (c) Sheet resistance vs oxygen partial pressure during growth. All points measured at 300 K. Blue symbols show the as-deposited interfaces while red shows the same samples after annealing in an oxygen rich atmosphere at 600°C for 4 hours. (d) Minimum thickness for 2DCG formation vs oxygen partial pressure during growth. Figures and caption adapted from Ref. 89.

conditions after annealing in an oxygen atmosphere. Finally, when Liu *et al.* grew a set of samples of various thicknesses and partial pressures, they found that there was no set critical thickness for the films and observed that for low oxygen partial pressures a 2DCG was formed even for 2 uc of aLAO.⁸⁹ This lack of a critical thickness showed that in these amorphous heterostructures the polar catastrophe mechanism did not meaningfully contribute to the 2DCG. Liu *et al.* then went on to show that in crystalline (001) LAO/STO heterostructures, the polar catastrophe and oxygen vacancies both contributed to the properties of the interface by performing systematic investigations sample resistance as a function of post growth annealing.⁸⁹ In later chapters, I will show that similar behavior occurs at the (111) LAO/STO interfaces,^{31,32} and by conducting a similar set of experiments, we can localize the anisotropy that we observe at the interface.^{31,32} Now, however, I will move to discussing some of the more interesting effects that have been seen at the (001) LAO/STO interface. These effects will prove to be one of the main motivations for moving towards an interface orientation that is not only more complicated to make, but far more complex in its properties.

2.2.2. Effects Seen at the Interface

Before I jump into the effects seen at the LAO/STO interface, I would like to again point out the significant differences between the 2DCG that forms at the interface and its closest analogues, other transition metal oxide (TMO) materials and the 2DCG that forms at the GaAs/AlGaAs interface.^{34,35,37,38,94,179} Other TMO interfaces and crystaline materials can show a host of effects; however, the amplitude and character of these effects are locked into the sample after growth and post processing.^{34,35,38,94,179} In LAO/STO heterostructures, not only can the properties of the 2DCG be changed during growth and post processing, but they can also be tuned via an electric potential applied to either the back of the STO or the top of the LAO. Going forward, I will notate this potential as V_g . Amongst other effects, V_g acts to populate/depopulate the interface with charge carriers, analogous to a field effect transistor, and is particularly effective when applied as a backgate on the STO, as at low temperatures the dielectric constant (ϵ) in STO is extremely large. This field effect tuning is identical to the method used in GaAs/AlGaAs heterostructures.^{37,97,98} Unlike those structures, LAO/STO heterostructures exhibit extremely strong electron-electron correlations, resulting in superconductivity,⁵⁻⁷ ferromagnetism,⁸⁻¹³ and large spin-orbit effects,^{7,16} all of which are tunable *in-situ* via V_g .^{14,15,20-23}

2.2.2.1. Superconductivity

At first glance, Reyren *et al.*'s discovery of superconductivity at the LAO/STO interface is not entirely surprising as STO itself has been shown to have a superconducting state.⁶ However, their further discovery that the superconducting gas was truly confined to the quasi-two dimensional interface, and transitioned to an insulating state in an applied magnetic field, has driven the furious pace of research through the past decade. Less than a year later, Caviglia *et al.*⁷ showed that not only could the superconducting state be tuned with a magnetic field, but it also could be tuned via V_g ,¹⁵ one of the first, if not the first, examples of gate tunable 2D superconductivity. Dikin *et al.*²⁰ conducted similar experiments; their results painted a clear picture of these superconducting properties and showed interesting parallels to the TMO cuprate superconductors. Figure 2.14(a)



Figure 2.14. Superconductivity at the (001) LAO/STO Interface: (a) Resistance vs temperature at various V_g , (b) V-I curves for the same set of samples and V_g . (c) Extracted T_c s and I_c s vs V_g showing the dome like behavior of the superconductivity in the sample. Adapted from Ref. 20

shows Dikin *et al.*'s results for the temperature dependence of sheet resistance, R_L , as a function of V_g . For positive back gate voltages the samples not only had lower normal state resistances, but also exhibited a higher superconducting transition temperature, $T_c \approx 100-105 \text{ mK}$.²⁰ On the other hand, at $-30V \leq V_g \leq 0$ V the samples no longer supported a zero resistance state, but still show a drop in resistance, and for even lower V_g the samples become weakly insulating. Similar behavior was seen in the V-I response shown in Figure

2.14(b), where critical current, I_c , was higher for more positive V_g ; however, in both sets of data the highest $V_g = 100$ V traces showed lower T_c and I_c , respectively.²⁰ When Dikin *et al.* mapped out the T_c and I_c as functions of V_g , they found both exhibited dome like behavior, similar to the superconducting domes observed as a function of doping in the cuprates, but in this case tuned by V_g , not growth.²⁰

2.2.2.2. Magnetism

In addition to superconductivity, ferromagnetic order was also observed at the LAO/STO interface.^{8–13} On its face this magnetism, unlike the superconductivity, was completely unexpected, as no similar effects have been observed in either STO or LAO for any value of oxygen vacancy doping. However, robust magnetism has been observed to exist at the interface using a wide variety of experimental probes;^{20–22,78–81,125} furthermore, local probes such as scanning SQUID microscopy have shown that this magnetism is spatially disordered.²¹ Unfortunately, such probes do not provide insight into the mechanism by which the magnetism came about or where it lived in the heterostructure. X-ray techniques such as XMCD, XAS, and XLD have been particularly helpful in elucidating the latter; oxygen vacancies are the key ingredient to finding ferromagnetic order in the LAO/STO samples.^{78–81} More specifically, the X-ray studies found evidence of magnetic Ti⁺³ in unannealed, oxygen vacancy rich LAO/STO samples.⁷⁸ These localized moments were almost completely quenched after annealing in an oxygen atmosphere, implying that the magnetism at the (001) LAO/STO interface lived almost exclusively in the oxygen vacancy defect states, not the carriers induced by the polar discontinuity.⁷⁸ Moreover, other groups have reported similar magnetic moments even in P-type interface samples where no mobile carriers exist, suggesting that the ferromagnetism can form even in the absense of conduction at the interface.^{80,81}

2.2.2.3. Coexistence of Superconductivity and Magnetism

While superconducting and magnetic phases are interesting in their own right, they are rarely found in the same material. This is because the Cooper pairs in conventional s-wave superconductors require anti-aligned spin moments, while ferromagnetic order requires parallel electron spins. However, it was discovered, first by Dikin *et al.*, that in (001) LAO/STO heterostructures both effects coexist at the 2-dimensional interface.²⁰ This coexistence was seen clearly in the measurements of T_c vs H, see Figure 2.15(a), where T_c was hysteretic and showed distinct dips at $\approx \pm 12$ mT; as a reminder, the superconducting properties of the sample can be seen in Figure 2.14.²⁰ The results of magnetoresistance measured as a function of V_g are shown in Figure 2.15(b) and also showed these hysteretic features, with peaks/dips at $\approx \pm 12$ mT.^{20,23} These peaks/dips were signatures of ferromagnetic order in the samples. More importantly, the data showed that this hysteretic behavior persisted even when the background resistance was reduced to zero, showing that the ferromagnetic order remains in a fully superconducting zero-resistance state.^{20,23}

A more subtle point in the MR data is that as the sample was tuned from the insulating to the superconducting state the dips in the magnetoresistance turned into peaks. Mehta *et al.* took this observation and combined it with the rate dependence of these features, and suggested they stemmed from a novel realization of charge-vortex duality at the interface.²³ Mehta *et al.*'s model for this behavior is presented schematically in Figure 2.15(c).¹²⁵ They proposed that the system consisted of a network of superconducting



Figure 2.15. Coexistance of Superconductivity and Magnetisim at the (001) LAO/STO Interface: (a) T_c vs H diagrams for the (001) LAO/STO samples measured by Dikin *et al.* at various V_g . (b) Sheet resistance vs perpendicular magnetic field at a variety of V_g as measured by Mehta *et al.* on the same samples measured by Dikin *et al.* (c) Schematic model of charge vortex duality at the interface. Figures adapted from Ref. 20 and Ref. 23 & 125.

islands with two ground states. The superconducting state where magnetic flux (contained in vortices) was localized and the superconducting Cooper pairs were delocalized, and the insulating state the vortices were delocalized and cooper pairs are localized.^{23,125} In the superconducting state, when the magnetic field was swept, and the ferromagnetic state switched direction, the vortices became delocalized, giving rise to the resistance peak seen in the data.^{23,125} On the other hand, in the insulating state, when the direction of the magnetic state was switched, it gave rise to a an electric field due to the changing magnetic field via Faraday's law of induction.^{23,125} This electric field built an electric potential up between the different superconducting islands, and once the voltage exceeded the electrostatic charging energies, Cooper pairs delocalized. This delocalization produced a dip in resistance as seen in Figure 2.15(b).^{23,125}

The above is only a terse accounting of the coexistence of superconductivity and magnetism at the interface of (001) LAO/STO, and while the topic could (and has) spanned an entire thesis,²³ I will now move into a discussion of the anisotropy that has been observed in the (001) LAO/STO heterostructures. This anisotropy will prove to be integeral to my observations of large in-plane anisotropy in the (111) LAO/STO heterostructures.

2.2.3. Anisotropy at the (001) $LaAlO_3/SrTiO_3$ Interface

An anisotropic response in the electrical transport and thermodynamic properties of materials is of great interest as it can be a sign of symmetry breaking. This symmetry breaking can lead to ferromagnetism, ferroelectric, and electric effects in the material. Anisotropy in the resistance is particularly interesting as it can be evidence of a nematic order in the system.^{34,35,37,38,94,96,179} Nematic order can manifest itself as a spin density wave in materials like iron-based superconductors^{34,35,38} or a charge density wave in certain fraction quantum Hall states,³⁷ however, just because resistance anisotropy exists in a material does not mean that these exotic phases are also present.^{105,106} The anisotropy can instead be due to the symmetry of the crystal lattice, shown most clearly by considering the resistivity tensor for the materials.^{96,99,100,102} The resistivity tensors are 3×3 matrices that can be generated from the symmetry elements of the crystal point groups and have both even and odd components in magnetic fields. For (001) LAO/STO heterostructures the symmetry of both the overall material and the interface is cubic (point group Pm3m) at room temperature and tetragonal (4/mmm) below ~ 105 K. Following the procedures in texts such as Akgoz and Saunders,^{100,101} Jones and March,¹⁰³ Harrison,¹⁰⁴ etc it can be found that at B = 0 the cubic tensor is,

$$\rho_{i,j}^{cubic}(B=0) = \begin{pmatrix} \rho_{x,x} & 0 & 0\\ 0 & \rho_{y,y} & 0\\ 0 & 0 & \rho_{z,z} \end{pmatrix}$$
$$\rho_{x,x} = \rho_{y,y} = \rho_{z,z}$$

and the tetragonal tensor is 100

$$\rho_{i,j}^{tetra}(B=0) = \begin{pmatrix} \rho_{x,x} & 0 & 0\\ 0 & \rho_{y,y} & 0\\ 0 & 0 & \rho_{z,z} \end{pmatrix}$$
$$\rho_{x,x} = \rho_{y,y} \neq \rho_{z,z}.$$

When $B_z \neq 0$ the two tensors become identical and are, given as,¹⁰⁰

$$\rho_{i,j}(B_z \neq 0) = \begin{pmatrix} \rho_{x,x} & \rho_{x,y} & 0\\ \rho_{y,x} & \rho_{y,y} & 0\\ 0 & 0 & \rho_{z,z} \end{pmatrix}$$
$$\rho_{x,x} = \rho_{y,y} \neq \rho_{z,z}, \ \rho_{x,y} = -\rho_{y,x}.$$

Reading off the above tensors it is readily apparent that for (001) LAO/STO there should be no in-plane anisotropy in the resistance at room temperature or low temperatures as in both cases $\rho_{x,x} = \rho_{y,y}$. However, there have been reports of not insignificant



Figure 2.16. Anisotropy with Respect to Step Edges: (a) Sample geometry with step and terrace structure and crystallographic a- and b-axes. (b) Resistance as a function of angle for various temperatures. Results are fitted with a sine function with a periodicity of 180°. Figure and caption taken from Ref 105.

resistance anisotropy at the (001) LAO/STO interface that stem from structural distortions at the interface.^{75,76,105,106} In what follows, I will highlight two examples of this anisotropy that will prove to be integral to my later results.^{105,106} First, Brinks *et al.*¹⁰⁵ observed a two fold anisotropy in the resistance of (001) LAO/STO heterostructures that was due to the atomic terraces that formed on the prepared STO substrate prior to deposition of the LAO.¹⁰⁵ Figure 2.16(a) shows the steps schematically, where 0° pointed along the steps, and 90° pointed transverse to the steps. These terraces were the result of a small miscut (< 0.05°) in the substrate that sloped the surface of the substrate and produced the terraced structures. Brinks *et al.* found that the resistance along Hall bar devices patterned at 90° had higher resistances than along Hall bar devices patterned at 0°.¹⁰⁵ Figure 2.16(b) shows this anisotropy most clearly for the traces that were taken at 5 K where the resistance transverse to the terraces was 4 times larger than along the terraces; however, a smaller anisotropy between 0° and 90° remained even at room temperature. Brinks *et al.* explained that this phenomena is in part due to increased scattering that occurs at the terrace edges. It is important to note that at $\pm 45^{\circ}$ to the terrace direction the resistances were identical.¹⁰⁵ In my samples the devices were fabricated such that they traversed the terraces at 45° ;³¹ thus, the anisotropy I observed could not be due to the atomic terraces.

In addition to the anisotropy caused by the atomic terraces, the structural transition to the tetragonal phase has been observed to be a source of anisotropy in the LAO/STO heterostructures.^{75,76,106} At first glance, this seems contradictory to the symmetry of the conductivity tensor for tetragonal crystal structures that I described above; However, it is important to remember that the structural transition from cubic to tetragonal does not occur uniformly across the single crystal.^{41,65,68,75,76,106} Instead, as I described in previous sections, without a symmetry breaking field this transition caused the formation of tetragonal domains with randomly oriented *c*-axes separated by ferroelectric domain



Figure 2.17. Anisotropy Due to Tetragonal Domains: (a) Resistance measured in the vertical (magenta) and horizontal (cyan) orientations. (b) Flux data for each domain configuration, plotted for one current orientation. Background was removed from images to emphasize features. Linear color bar spans [-2.39, 2.43] $-\phi_0/A$. (c) Resistance anisotropy, observed at 4.2 K (full circles), but not at higher temperatures (empty circles). Figure and caption adapted from Ref. 106.

walls. Frenkel *et al.* used polarized light microscopy coupled with a scanning SQUID technique to first confirm that the tetragonal domains existed and then mapped the current distribution in the samples.¹⁰⁶ They correlated the spatial current distributions shown in Figure 2.17(b) to simultaneous measurements of the resistance shown in Figure 2.17(a) and found that current flowed preferentially along the domain walls.

Concomitant with the preferential direction for current flow, the resistance along the direction parallel to the domain walls was found to be lower than in the direction perpendicular to the walls.¹⁰⁶ This is shown most clearly in Figure 2.17(a), where the pink/(blue)

symbols correspond to the resistances in the direction parallel/(perpendicular) to the domains shown in Figure 2.17(b). They plotted the anisotropy as $2|R_{\parallel} - R_{\perp}|/(R_{\parallel} + R_{\perp})$ is shown in Figure 2.17(c) and indicated that while large amounts of anisotropy existed at 4K (black circles) it did not exist above the 105K transition (white circles). Furthermore, every time the temperature was cycled through the structural transition temperature (105 K) the domain configuration reformed randomly as shown along the x-axis of Figure 2.17: this random reconfiguration lead to randomness in both anisotropy direction and amplitude.¹⁰⁶

In the previous sections I have detailed the origins of the 2DCG at the (001) LAO/STO interface, the effects seen there, and the signatures of anisotropy at the interface. While all of the effects are interesting on their own, it is the *in-situ* tunable interplay between the effects that has continued to drive fervent research in the material a decade after the first discovery. In the next section I will describe the properties of the (111) orientation of the LAO/STO, which as recently been shown to host a 2DCG. The observations made the (001) orientation of the LAO/STO interface to guide not only characterization of the (111) LAO/STO interface, but help us separate new effects from an already overwhelming large phase space.

2.3. The (111) $LaAlO_3/SrTiO_3$ Interface

2.3.1. Crystal Structure and Growth of LAO/STO Interfaces Beyond the (001)

While LAO/STO interfaces have shown a host of interesting effects, these effects, until 2012,²⁴ have only been observed in the (001) orientation of the interface. However, other orientations of the LAO/STO interface, such as the (110) and (111) orientations, have been

predicted to show a number of effects even more exotic than those described in the previous section.^{28,107,108} The (111) LAO/STO interface has proven to be particularly fascinating due to the prediction that bilayer (111) TMO heterostructures could function as the fundamental building blocks for 2D topological insulators. Unfortunately, both the (110) and (111) interfaces pose unique challenges to realizing a 2DCG at the interface.^{109–114}



Figure 2.18. The Four Possible LAO/STO Interfaces: The sketches display (001), (110)- and (111)-oriented LAO/STO interfaces, along with oxide amorphous layers (LAO, STO, YSZ) interfacing (110)-oriented STO, all of them exhibiting high-mobility conduction. Figure and caption taken from Ref. 24.

Multiple groups found that the primary challenges for growing of conducting interfaces in these orientations were: (a) achieving a single species of atomic termination (i.e. TiO_2 , SrO, etc); (b) forming a stable substrate interface with air and/or a vacuum without structural or electronic reconstruction; and (c) forming a stable interface between the substrate and the film material.^{110–115} The two orientations each posed different problems, which can seen by simply examining the crystal structures of each heterostructure shown in Figure 2.18. For the (110) structure, there were problems more fundamental



Figure 2.19. Reconstruction Possibilities for the (111) Ti Terminated Interfaces: A ball and stick model of four possible (111) surface reconstructions: the pristine Ti^{+4} interface, an interface with one TiO per surface unit cell, a trigonal TiO₂ reconstruction, Ti_2O_3 terminated interface, and an interface with 3 TiO per surface unit cell. Figure adapted from Ref. 109.

than the materials growth challenges;^{24, 27, 112} namely, the interface was non-polar and was believed to be incapable of exhibiting a 2DCG based on the polar catastrophe.²⁴ For both the (110) and (111) heterostructures, it was discovered that atomically terminated STO substrates could be obtained via careful chemical etching and annealing, thus satisfying condition (a). Furthermore, at least for the LAO/STO heterostructures condition, (c) was found to be easily satisfied.^{24,115}

As I previously discussed, the (001) 2DCG forms between TiO₂ terminated STO and LaO terminated LAO due to the combination of a polar discontinuity and oxygen vacancies. However, the STO in the N-type (110) and (111) heterostructures is terminated with O_2^{+4} and Ti^{+4} , ^{24, 109–111, 113} respectively; both of which were found to be extremely unstable to surface reconstructions^{109–112,115} in air or vacuum, as the STO wants to passivate its surface, thus breaking condition (b). The (111) interface in particular was observed to have a vast number of low energy surface reconstructions,^{109–111,115} Figure 2.19 shows, schematically, the 4 lowest energy reconstructions that have been calculated via DFT for the N-type interface. The first panel shows the perfect Ti⁺⁴ terminated interface, which would support a polar catastrophe scenario; however, this interface was extremely reactive and is subsequently passivated by forming one of four titanium oxide surfaces.¹⁰⁹ The first reconstructed interface is the 1xTiO termination is formed by absorbing an oxygen atom to the surface, and was a fairly high energy surface as it does not fully passivate the surface.¹⁰⁹ The most energetically favorable surfaces were the TiO_x rich surfaces shown in the bottom row, where the Ti_2O_3 and 3(TiO) surfaces were formed in more reducing atmospheres, while the TiO_2 surface was formed in more a oxidative atmosphere.¹⁰⁹ The lowest energy structure was, perhaps unsurprisingly, the TiO_2 surface structure, which had an energy of formation nearly 4 eV lower than the Ti^{+4} surface and, as previously discussed, was very stable at room temperature and in any atmosphere, but had the lowest energy in oxidative atmospheres.¹⁰⁹ Not shown in the figure are the SrO teminated surfaces, which also had very low energies of formation in ambient atmospheres, 3.75 eV below the pristine Ti terminated surface. In reality, a mixture of the TiO_2 and SrOsurfaces have been observed on as-grown (111) STO substrates. The SrO surface was

removed during the hydrofluoric acid etching process, which is used as part of the processing required to achieve an atomically flat surface for growth, while the TiO_2 remained as it is not as soluble in hydrofluoric acid.^{24,110–115} The samples were then annealed, typically at 1000 °C, in a pure oxygen atmosphere, which further nucleated the TiO_2 surface. This surface evolution has been observed by a combination of AFM and X-Ray characterization techniques,^{111–114} which revealed that although a near perfect TiO_2 terminated surface could be achieved, SrO islands reformed over the span of days to weeks, again demonstrating the instability of this surface.^{110–115}

Despite these challenges, Herranz *et al.*²⁴ found that they could indeed grow both (110) and (111) heterostructures with conducting interfaces. They did this by growing LAO on annealed, atomically flat (110) and (111) substrates via PLD. The growth was conducted at 850 °C in an oxygen atmosphere with a partial pressure of 10^{-4} mbar, followed by an anneal in a 200 mbar O₂ atmosphere after growth was complete.²⁴ The anneal was performed to remove oxygen vacancies formed at the interface and in the bulk STO during growth.²⁴ Their results showed that like the (001) LAO/STO interface both the (110) and (111) STO samples displayed a critical dependence on LAO film thickness as shown in Figure 2.20. Both the (110) and (111) interfaces showed a sharp rise in conductivity after 7 and 9 mono layers (ML) of LAO were grown, respectively, indicating that regardless of the STO termination a polar catastrophe type of electronic reconstruction was taking place.²⁴ Unlike the (001) interface, the conductance of the (111) interface was found to degrade rapidly with increasing LAO thickness, and became 3 orders of magnitude more resistive as LAO thickness was increased from 9-23 MLs.²⁴ This degradation became even more apparent when the LAO/STO heterostructures were



Figure 2.20. Conductance measured at room temperature as a function of the LAO overlayer thickness for interfaces oriented along [110], [001], and [111] directions. Figure and caption adapted from Ref. 24.

measured as a function of temperature for various LAO film thicknesses. Figure 2.21(b) shows that as the (111) samples were cooled to 4 K, they transitioned from metallic behavior for 9 ML thick samples to weakly insulating behavior with the addition of just one ML (10 ML).²⁴ As the LAO thickness was increased, the insulating behavior was greatly enhanced with exponentially increasing resistance below $\approx 45 \text{ K}$.²⁴



Figure 2.21. Sheet Resistance vs Temperature vs Layer Thickness for the (110) and (111) Directions: Temperature dependence of the sheet resistance of LAO/STO interfaces of different LAO overlayer thickness, oriented along (a) [110]- and (b) [111]- crystallographic directions. Figure taken from Ref. 24.

This thickness dependent behavior has not been observed for (001) or (110) samples. This may be due to the more complicated interface morphology and conduction mechanisms. Beyond the Gordian knot that is the origin of conduction at the (110) and (111)interfaces, both interfaces display a wealth of behaviors that have not been observed in the (001) LAO/STO interfaces. In the next section, I will leave the (110) interface behind and describe the work done on characterizing the band structure of the (111) 2DCG, as well as the unique effects predicted to live there.

2.3.2. Band Structure and Symmetry at the interface

Although I have established that the (111) interface can be made conductive, the question remains as to why this interface is interesting, and why it is worth the vast amount of effort necessary to engineer the conducting interface. The answer to this question lies in the crystal symmetry at the interface. In the (001) interface this symmetry is cubic, at least at room temperature,^{2,27,87} for clarity this is shown schematically again in Figure 2.22 (a). In the (111) LAO/STO interfaces the symmetry at the interface is hexagonal.^{24,26,27}

You can most easily see the hexagonal symmetry in Figure 2.22(a) and (b), where the grey triangular planes in (a) show cross cuts of the first two ML of Ti atoms at the (111) STO surface. Figure 2.22(b) shows the top down view of these Ti atoms where the largest, lightest grey, atoms are at the interface and are labeled Ti 1. Moving downward, the remaining atoms in the diagram correspond to the Ti atoms at the 2nd and 3rd layers below the interface, represented by the medium/(dark grey) and small/(black) spheres, respectively.²⁷ These three sets of atoms form a hexagonally symmetric set of planes that has been dubbed the "strongly correlated equivalent of graphene,"²⁸ and has driven many of the studies, both theoretical and experimental, of the system.^{26,27,29–33,39,40} Further characterization of this interface can be done by looking at the two orthogonal in-plane crystal directions: the [$\bar{1}\bar{1}2$] and [$1\bar{1}0$] directions.²⁷ The [$\bar{1}\bar{1}2$] points along sets of nearest neighbor atoms separated by the cubic lattice constant *a*, while the [$1\bar{1}0$] points along



Figure 2.22. The (001) and (111) STO Crystal Structures and Fermi Surface Diagrams: (a) Unit cell of SrTiO₃ with inequivalent (111) planes indicated in grey. (b) Top view of three consecutive Ti⁺⁴ (111) layers. Each of the three t_{2g} orbitals are shown on the honeycomb lattice, formed by two consecutive layers (dark grey lines), to illustrate their rotational symmetry. The d_{xz} orbital is shown in all three layers with large (t₁) and small (t₂) nearest neighbor hoppings indicated. (c) Sketch of the bulk FS of STO cut by the (001) plane. (d) The same bulk FS viewed down the [111] axis. A cut in the (111) plane through the Γ point is indicated by black lines to illustrate its different shape and size from the projection of the FS on the (111) surface plane. Figures and caption taken from Ref. 27.

the next nearest neighbor atoms separated by $\sqrt{2}a$.²⁷ The (111) LAO/STO interface, as well as the STO surface, lacks C_6 symmetry because of the layered nature of the interface; and instead, exhibits C_3 symmetry at room temperature. The most immediate consequence of the interface's symmetry is a more complex Fermi surface, shown in Figure 2.22 (c) and (d) for the (001) and (111) heterostructures, respectively.²⁷ As a reminder, in the (001) heterostructure the d_{xy} orbitals are at a lower energy and have higher mass in the z-direction. The same Ti $d_{xy,xz,yz}$ orbitals make up the Fermi surface in (111) heterostructure, ^{26–28,107} but in this case all three orbitals are nominally degenerate at the Γ -point in the z-direction, the [111] direction in this interface.^{26,27} Away from the Γ -point, the bands in the (111) plane have the same C_3 symmetry as the crystal structure with lobes in the $\langle \bar{1}\bar{1}2 \rangle$ directions, which corrispond to the Ti t_{2g} bands, and nodes in the $\langle 1\bar{1}2 \rangle$ lobes with their weaker dispersion have a much higher mass than the stronger dispersing nodes in the $\langle 1\bar{1}0 \rangle$ directions.^{26,27}

McKeown-Walker *et al.*²⁷ and Rodel *et al.*²⁶ have measured the ARPES response of 2DCGs (111) STO surfaces.Figure 2.23 (a) and (b) show the Fermi surface as measured by Rodel *et al.*,²⁶ where panel (a) shows a view along the surface normal. The results clearly showed the 120° rotational symmetry, both in the nodes along the $< 1\overline{10} >$ directions from $K' \to \Gamma \to K$,²⁶ as well as the weaker dispersing lobes in the $< \overline{112} >$ directions from $M' \to \Gamma \to M$.^{26,27} Figure 2.23(b) shows a cut along the $< \overline{112} >$ directions. As expected, near the Γ -point Rodel *et al.* observed the light and the heavy bands stemming from the [$\overline{112}$] bands were degenerate within their measurement resolution, $\approx 5 \text{ meV.}^{26,27}$ Away from the Γ -point, they found the masses were dramatically different.^{26,27} They found that along the more weakly dispersing [$\overline{112}$] direction the masses were 8.7 times heavier than the bare electron mass for the heavy band, while in the [$1\overline{10}$] direction the mass was roughly the bare electron mass for the heaviest band in that direction.^{26,27}

McKeown-Walker *et al.* also measured the ARPES response in (111) STO surfaces:²⁷ however, unlike Santander-Syro's results, which were measured on perfectly insulating substrates, the samples measured were lightly doped with Nb.²⁷ This doping was done, ostensibly, for contrast proposes, and the surface state was then created via a combination of *in-situ* cleaving and UV oxygen vacancy doping.²⁷ Despite these differences, the (111)STO surfaces measured by McKeown-Walker *et al.* showed results which at first glance were nearly identical to Santander-Syro *et al.*'s: Figure 2.23(c) & (d) show the results measured along the $[1\overline{1}0]$ direction and $[\overline{1}\overline{1}2]$ direction, respectively.²⁷ Figure 2.23(d) shows that the [112] band spanned roughly the same momentum and energy ranges as the heavy $[\bar{1}\bar{1}2]$ bands in Figure 2.23(b). In McKeown-Walker's results, lighter $[\bar{1}\bar{1}2]$ bands were assigned to the bulk states that existed due to the Nb dopants; nevertheless, these "bulk" bands were identical to the light $[\overline{1}\overline{1}2]$ bands that were seen in Santander-Syro's insulating samples,^{26,27} despite those samples not having bulk states. More strangely, when McKeown Walker measured the oxygen vacancy dependence of the 2DCG, they found that the bands, including these "bulk" bands, disappeared when the 2DCG disappeared.²⁷ This implies that the light [112] bands should have been associated with the surface states, not the bulk substrate. Such discrepancies will require further measurements to fully elucidate the origins of these bands. In addition to the ARPES measurements, both groups also performed tight-binding calculations in order to determine a rough band structure for the surface states.^{26,27} The results of McKeown Walker's calculations were in good agreement with Santander-Syro's results and are shown in Figure 2.23(e) & (f).^{26,27} In both cases the calculations predicted a slight splitting in the light and heavy bands along along both in-plane directions at the Γ -point due to confinement at the interface.^{26,27}



Figure 2.23. (111) STO ARPES Results and Tight Binding Calculations: (a) Fermi surface map around the Γ -point as measured by Santander-Syro *et al.* (b)Energy-momentum map across the Γ -point point along the $[\bar{1}\bar{1}2]$ directions. (c),(d) Energy-momentum dispersion along the $[1\bar{1}0]$ and $[\bar{1}\bar{1}2]$ directions as measured by McKweon -Walker *et al.* (e),(f) Calculated band dispersion along the $[1\bar{1}0]$ and $[\bar{1}\bar{1}2]$ directions, showing three confined 2DEG subbands and a "ladder" of states above E_F due to the finite size of the supercell. Figure and captions adapted from Refs. 27 and 26.

Unfortunately, neither this lack of degeneracy nor any spin splitting were observed within the experimental resolutions: the latter being one of the core phenomena that have been predicted at the interface.^{28,107}

The last point to consider, before moving to the predicted effects at the interface, is whether this more complex crystal would yield any resistance anisotropy simply from its symmetry. As I mentioned previously, the symmetry at the interface is trigonal, C_3 . Again following the procedure of Section 2.2.3, the resistivity tensor at B = 0 is¹⁰⁰

$$\rho_{i,j}^{C_3}(B=0) = \begin{pmatrix} \rho_{x,x} & 0 & 0\\ 0 & \rho_{y,y} & 0\\ 0 & 0 & \rho_{z,z} \end{pmatrix}$$
$$\rho_{x,x} = \rho_{y,y} \neq \rho_{z,z}.$$

When $B_z \neq 0$ the tensor becomes,¹⁰⁰

$$\rho_{i,j}^{C_3}(B_z \neq 0) = \begin{pmatrix} \rho_{x,x} & \rho_{x,y} & 0\\ \rho_{y,x} & \rho_{y,y} & 0\\ 0 & 0 & \rho_{z,z} \end{pmatrix}.$$

Thus with or without magnetic field, the two in-plane crystal directions, in this case the $[1\bar{1}0]$ and $[\bar{1}12]$ directions, should be completely isotropic. This makes the observations of anisotropy in the system that I will describe later completely unexpected from a simple symmetry perspective.^{29–33}

2.3.3. Effects Predicted at the (111) LAO/STO Interface

Much of the interest in the (111) oriented LAO/STO interface has stemmed from predictions of a variety of intriguing phenomena such as ferroelectric phases,²⁸ coexistence of the ferroelectric and ferromagnetic phases,^{28,108} topological phases,²⁸ as well as nematic spin density wave states.¹⁰⁷ In this section, I will briefly discuss the predictions of Doennig et $al.^{28}$ and Boudjada et $al.^{107}$

Doenig et al. studied the band structure of (111) LAO/STO by performing DFT calculations on LAO_M/STO_N superlattices grown on either LAO or STO substrates.²⁸ Bilayer superlattices were chosen, both for the easy control of the built in strain and symmetries, as well as the close emulation of experimentally achievable quantum well structures. They performed their calculations at zero temperature for a variety of frozen in symmetries and strains using the Linearized Augmented Plane Wave (LAPW) method.²⁸ Doenig et al. found that for superlattices grown on LAO, ferroelectric order coexisted with a charge ordered ferromagnetic state that was made more interesting by the explicit existence of hole pockets in the Fermi surface.²⁸ Having said that, the structures discussed thus far in this thesis involved LAO grown on STO, thus I will focus on the superlattices grown on STO. In this case, Doenig et al. found that, for heterostructures with N=2and inversion symmetry, the system displayed a Dirac point at the zone corner K-point that was pinned at the Fermi energy.²⁸ This Dirac point, shown in Figure 2.24(a) was the result of a topological insulating phase that was protected not by spin-orbit coupling, as in other topological insulators, but instead by the equivalence of the Ti sites, similar to the protected points in graphene.²⁸ Doening *et al.* further found that when inversion symmetry is lifted, the system reverts to C_3 symmetry, and the Dirac point was no longer protected. This caused a charge ordered phase to nucleate in the system alongside ferroelectric and ferromagnetic order. The charge ordered state is shown schematically in Figure 2.24(b) where the electrons are transferred to the lower Ti atoms giving rise to the C_3 symmetry, and a flat electron band $\approx 0.8 \text{ eV}$ above the Fermi energy.²⁸ These flat


Figure 2.24. (111) LAO/STO Multilayer Calculations: (a) Superlattices at for a_{STO} for N = 2. For the inversion symmetric interfaces the system is a Weyl semimetal with Dirac points (DP) at K, K'as in graphene.(b) Allowing breaking of inversion symmetry results in in-equivalent interfaces. Figure and caption adapted from Ref. 28.

bands have been predicted to give rise to an anomalous fractional quantum Hall state, and have received a large amount of theoretical attention.^{28,116–118} As temperature was increased the charged ordered insulator was found to melt and give rise to conduction with a rich variety of effects.²⁸ Unfortunately, the results were not readily extensible to the simple LAO/STO heterostrucutres studied in this thesis: provided the correct symmetries and strains are maintained, similar orders are expected to exist.²⁸



Figure 2.25. (111) LAO/STO Phase Diagram Calculations: (a) Phase diagram of the (111) 2DEG at low temperature, T = 0.02t, as a function of the Hubbard repulsion U/t and Hund's coupling J/t. The different metallic phases are paramagnetic (PM), ferromagnetic (FM), and three types of spin-density waves: SDW1 (collinear stripe), SDW2 (double-Q order), and SDW3 (triple-Q order). Fluctuations convert SDW1 and SDW2 into electronic nematic phases. Figures and captions adapted from Ref. 107.

Boudjada *et al.* have used the random phase approximation coupled with mean field theory (RPA/MFT) to study (111) LAO/STO 2DCGs, by first calculating the bands using a tight-binding model of the Ti t_{2g} orbitals on a triangular lattice. These calculations were similar to the calculations performed by Rodel *et al.* and McKeown-Walker *et* $al.;^{26,27,107}$ however, they then performed RPA/MFT analysis to examine the electronic correlations in the material, including both orbital and spin interactions. The results of these calculations allowed them to build a phase U - J phase diagram, where U is the amplitude of the on-site repulsion energy and J is the Hund's coupling. This phase diagram is shown in Figure 2.25(a) and showed that for low $U_{1} < 2t$, and J < 0.6t the system was in a paramagnetic state, while for U > 2t and J > 0.6t the system was in a ferromagnetic state.¹⁰⁷ While both states are interesting in their own right, a more interesting set of three spin density wave states were found to exist at high U and intermediate J. These spin ordered states melt in the presence of disorder and/or temperature leading to a charge nematic order that may be stabilized by the existence of spin-orbit coupling (SOC): however, since SOC was not explicitly included in the interaction Hamiltonian the dependence of the charge nematic order on SOC amplitude was not investigated.¹⁰⁷ Boudjada *et al.* described how this nematic state affects the transport characteristics by calculating the Drude conductivity. They simplified the conductivity calculation by first assuming that the nematic order parameter ψ_n is purely charge like and has no spin component, as would be the case in the presence of disorder. In addition, they also suppressed any intra-orbital hopping.¹⁰⁷ With these simplifications, the conductivity tensor was the sum of the 3 orbital components, $\hat{\sigma} = \sum_i \hat{\sigma}_i$, i = 1, 2, 3, where the *i* indexs the Ti t_{2g} orbitals. Furthermore, in the Drude model each element of the $\hat{\sigma}$ was proportional to the orbital carrier densities n_i . In terms of in-plane Cartesian coordinates x, y they found the conductivity to be¹⁰⁷

(2.1)
$$\hat{\sigma} \approx \frac{3}{2}(\sigma_x + \sigma_y) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{1}{2}(\sigma_x - \sigma_y) \begin{pmatrix} Re\psi_n & Im\psi_n \\ Im\psi_n & -Re\psi_n \end{pmatrix}.$$

The nematic order parameter was approximated by $\psi_n \sim ((n_1 - n_0) + \omega(n_2 - n_0) + \omega'(n_3 - n_0))$, where n_i is the carrier density along along each of the Ti t_{2g} orbitals and n_0 is the average orbital carrier density.¹⁰⁷ The two Cartesian directions corresponded

to the direction along one of the orbitals, the $[\bar{1}\bar{1}2]$ direction, and the direction along one of the overlap nodes, $[1\bar{1}0]$ direction. Their conductivity matrix showed that increased conductivity is expected along the $[\bar{1}\bar{1}2]$ direction in the nematic state. In addition, they also speculated that this nematic state would strongly effect any superconducting state at the interface. These effects included causing anisotropy in the shape of any vortices at the interface as well as producing an anisotropic critical current.¹⁰⁷

In the next chapter, I will describe the techniques I have used fabricate, and characterize the (111) LAO/STO interfaces used in this thesis. These techniques range from X-ray and surface characterization to a variety of high sensitivity low noise electrical transport measurement techniques. I will also discuss some of the difficulties presented by the (111) LAO/STO interfaces and what techniques I used to circumvent them.

CHAPTER 3

Experimental Techniques and Background

In this chapter I will discuss the experimental techniques used to characterize the (111) LAO/STO samples and gather the data presented later in the thesis. While most of this review will focus on the technical aspects of these techniques, I will on occasion give historical or theoretical context to explain why the techniques are being used. As many of the techniques and processes employed in this work have been developed over many generations of graduate students,^{119–125} I will not extensively review the methods covered in past theses unless expansion is necessary or procedures have changed.

I will begin the chapter by giving a review of the lithography process used to fabricate the (111) LAO/STO heterostructures as some of the parameters and protocols are different from those reported in past theses. I will also discuss the Ar ion milling procedures necessary to produce conducting devices on bare (111) STO. I will then describe the materials characterization techniques that are crucial to the claims that I will make later in this work. These techniques include the X-ray characterization of the surface crystal directions, AFM characterization of the atomic terrace morphology, and the use of photoluminescence to measure the relative oxygen vacancy concentration in the LAO/STO heterostructures. Finally, I will describe the electrical measurement techniques used in this thesis, including a technique for measuring the capacitance in 2D materials.

3.1. Device Fabrication

Device and/or sample fabrication is one of the first steps to any experiment in condensed matter physics and transition metal oxide heterostructures present a number of challenges to the sample growth and device fabrication processes. The LAO/STO substrates for our devices were obtained from Professors Venkatesan's and Ariando's groups at the National University of Singapore (NUS), and were grown by pulsed laser deposition (PLD). PLD uses a UV laser to ablate the surface of a target material causing it to vaporize and expand towards the sample in a plume of plasma.^{126,127} When the plume reaches the sample it recondenses in a thin layer on the surface of the material. While similar to other physical vapor deposition techniques like sputtering, PLD offers a number of advantages in achieving repeatable epitaxial heterostructures.^{126,127} These advantages include the preservation of stoichiometry in the fairly complicated perovskite compounds, providing a uniform epitaxial film thickness over relatively large areas, and a fairly high yield. The NUS groups have a multitude of publications detailing the sample PLD process, *in-situ* characterization, and post growth characterization.^{16,25,92,128} In addition, Manan Mehta's thesis has a great review of the overall process.¹²⁵ Thus I will not be covering the process in depth. I will, however, highlight a change in substrate pre-processing that allows for more consistent termination (111) STO substrates.

In the (001) LAO/STO structures, the STO substrate was prepared by etching in Fisher-Scientific 10:1 buffered oxide etch (BOE) for 90 seconds followed by a rinse in deionized water (DI) and annealing in an oxygen atmosphere for 6 hours at 1000° C. However multiple groups have found that on (111) STO this process leads to the nucleation of SrO islands after annealing.^{110,135} These were removed by another etch in BOE for 90 seconds and rinsed again in DI water, which removed the SrO. The samples were then placed in PLD and LAO was deposited on top of the STO while *in-situ* RHEED was used to monitor the growth thickness and quality. All of the samples that I have measured for this thesis had 20 uc of (111) LAO deposited at 600° C in an oxygen partial pressure of 1 mTorr of oxygen. Our collaborators at NUS did not conduct an *in-situ* post growth oxygen anneal, ensuring that a large number of oxygen vacancies were present at the interface.

3.1.1. Lithography

The first step in the device fabrication process after receiving the samples from NUS was to remove the packaging debris as well as the silver paint from the backside of the sample. Drs. Zhen and Han at NUS use this silver paint to affix the sample to a probe station used for room temperature measurements prior to shipment; unfortunately, improper removal of this conductive paint has in the past lead to surface conduction due to contamination. This surface conduction was not due to the 2DCG at the interface, and was nearly impossible to remove after further fabrication steps.

The procedure to remove these contaminants as follows, (a) spray the backside of the sample with acetone for 2-4 minutes depending on the amount of silver paint. Do not let the sample soak in a beaker of acetone. (b) immediately spray the sample with iso-propyl alcohol, IPA, to prevent the acetone from drying on the surface, which would leave an organic residue. (c) Use dry N₂ to remove the IPA from the surface. (d) Rinse the sample with 2 M Ω DI water to remove any residual ionic contaminates. (e) Rinse the sample with IPA to remove DI water residue and then dry the sample again with N₂. (f) With a hand held multimeter check the surface conduction by gently pressing two needle probes to the surface. The resistance should measure > 40 M Ω , if it does not repeat steps (a)-(d) until it does. Once the silver paint has been removed, move to cleaning the surface by, (f) ultrasonicating the samples in DI for 5 minutes, (f) ultrasonicating the samples in acetone for 5 minutes, (g) spray the sample with IPA to remove the acetone, and (h) ultrasonicate in fresh IPA 5-minutes. Finally, (i) dry the sample with dry N₂.

At this point, the sample is ready for the first lithography steps used to define the Hall bar, deposit metal contact pads, and, if necessary, add additional control devices or gates. Figure 3.1 shows a schematic of the lithography required for the milling process, starting with the cleaned sample in Figure 3.1(a).

- (1) Spin coat the samples with a positive resist using a borosilicate pipette to apply the resist. For the Hall bar devices, use a positive photoreisist such as Microposit S1813.¹ In this case we use only a single, imaging, resist layer to minimize undercut in the resist, which would decrease the spatial resolution of the milling step. For these particular devices, S1813 is spun at 3000 rpm for 40 sec yielding a film with a uniform thickness of 1.2 μm. These spin parameters were chosen based on the recipes found the the S1813 resist spec sheet. Figure 3.1(b) shows this step schematically.
- (2) Place the sample in an clean glass dish and bake in the Clean 100² oven for 30 minutes at 110° C to drive the solvent out of the resist.
- (3) Expose the sample using the using the homemade contact aligner,¹²¹ flood light, and Hall bar mask. The mask is a made from a soda lime plate and chromium oxide mask metal. The sample is held to the mask by vacuum provided by the

¹Rohm and Haas, 'MicropositTM S1800TM Series Photo Resists', *Microchem.com*, (2006).

²Lab-Line Instruments, Inc., Melrose Park, IL.



Figure 3.1. Schematic representation of the lithography steps for the etch process. Orange, blue, red, and grey blocks in the image correspond to the STO, LAO, photoresist, and photomask respectively.

house vacuum. The flood light bulb is currently a GE 150 watt halogen flood light bulb with a textured glass lens and is placed 1 m from the contact aligner. For this bulb an exposure time of 10 minutes is required to achieve a good exposure, however it should be noted that different bulbs *will* require different exposure times.

(4) Develop the sample in Microposit MF319 developer³ for 55 sec at 24° C, then rinse the sample for 30 sec in DI water. I apply the developer by placing the

 $^{^3{\}rm Microposit}$ photodeveloper, distributed by Microchem Corp., Westborough, MA http://www.microchem.com/

sample in a beaker of developer, this insures that the sample is always in excess developer.

- (5) Dry the samples with dry N_2 ,
- (6) Ion mill the sample in the Chandrasekhar group's homemade Ar ion mill. In later sections I will discuss in some depth the parameters used for milling and the parameters used for inducing a 2DCG at the interface. Figure 3.1(e) shows this schematically.
- (7) Remove the resist mask from the milled sample using an acetone bath. Depending on the ion milling parameters used, the sample may heat to high temperatures, which will harden the resist. In this case an ultrasonic bath may be necessary to remove the hardened resist.
- (8) Once the resist is removed, rinse the sample with IPA from a squeeze bottle and dry with N₂. The Hall bar devices are now complete and could be measured in this state. Figure 3.1(f) shows this schematically.

As I mentioned above, the etching step completely defined the Hall bar devices used in this thesis. However, additional lithography layers are used to place metal contacts on the Hall bar devices as well as to define control structures, which are used to ensure that the effects observed are due to the 2DCG and not systematic errors, such as surface conduction between Hall bar devices. The metal pads are used as guides for the eye when electrically contacting the samples with aluminum wire bonds and were fabricated on the sample using the following steps:



Figure 3.2. (Schematic representation of the lithography steps for the metallization process. Orange, blue, red, green, yellow, and grey blocks in the image correspond to the STO, LAO, undercut photoresist, imaging photoresist, Ti/Au bilayer, and photomask respectively.

- (1) In this process an undercut layer is needed to ensure clean lift off of the metal layer. For the Hall bar devices, I used the undercut resist Microposit LOR 7B⁴. Apply the resist using a borosilicate pipette to apply the resist and spin at 4000 rpm for 30 seconds. These parameters were taken from the suggested recipe in the manufacture's specification sheet and yields a thickness of $3.2 \ \mu m$.
- (2) Bake in the Clean 100 oven for 40 minutes at 170° C to drive the solvent out of the resist.

⁴Microchem Corp., Westborough, MA http://www.microchem.com/

- (3) Spin coat the samples with a positive imaging resist using a borosilicate pipette to apply the resist following step one from the etch lithography process.
- (4) Bake the samples per step (2) in the etch lithography process. Figure 3.2(a) shows this stem schematically.
- (5) Align the Hall bar device and second pattern that contains the contact pads using the Suss MA/BA6 mask aligner⁵ housed in the NUFAB clean room⁶ and Hall bar mask. Expose the sample using the UV lamp (with λ = 365 nm) for 12 seconds. These exposure parameters were chosen based on dosage tests performed on glass substrates.
- (6) For S1813/LOR 7B bilayers, develop the sample in MF319 developer for 55 sec at 24° C and then rinse the sample for 30 sec in D.I. water. Figure 3.2(c) shows this schematically.
- (7) Dry the samples with dry N_2 ,
- (8) Use the Joetek or Denton e-beam evaporators to deposit metal contact pads/control devices.¹²¹ In the Jotek e-beam evaporator, the chamber should pump down to 6× 10⁻⁷ Torr in 2 hours. If it does not, clean the chamber, check that the *in-situ* etcher gas supply is closed, or change the diffusion pump oil.
- (9) Deposit the desired metals on the samples. Normally a bilayer of 3 nm of Ti and 30 nm of Au is used, where the Ti acts as a sticking layer. With the shutter closed pre-bake both crucibles to remove any water or organic materials and then let the chamber pump down to 4-5× 10⁻⁷ Torr. If extremely clean metallization is required the chamber can be pumped to its base pressure of 5× 10⁻⁸ Torr.

⁵SUSS MicroTec AG, Garching, Germany, http://www.suss.com/en.html ⁶NUFAB, Evanston, IL,http://nufab.northwestern.edu/

(10) Begin depositing Ti, first pre-evaporating 4-10 nm of Ti on to the chamber walls with the shutter closed at a rate of 0.6 Å/s. During the pre-evaporation the chamber pressure should remain below 1× 10⁻⁶ Torr. Once the pre-evaporation is complete, open the shutter and deposit 3 nm of Ti on the sample. After 3 nm of thickness is recorded on the quartz thickness monitor close the shutter and ramp down the e-beam current. After the Au crucible is positioned in the beam path repeat the process, this time pre-evaporating 5 nm and depositing 30 nm of Au at 2.4 Å/s. Figure 3.2(d) showes this process schematically.

It is important to monitor the pressure during these steps, ensuring the chamber pressure remains below 1×10^{-6} Torr. If it does not, inspect the crucible for contamination and perform any necessary chamber cleaning or evaporator maintenance.

- (11) Let the sample and evaporator fully cool in vacuum before venting the chamber.If you do not fully cool the sample, clean lift off will be difficult.
- (12) Remove the metal and resist mask from the sample using a steady stream of acetone from a squeeze bottle to the surface of the sample. This should take less than 5 minutes, rinse with IPA, and dry with N₂. Then strip the LOR 7B by soaking the sample in Microposit 1165 resist stripper⁷ heated to 65° C for 30 minutes. Rinse the sample with DI water to remove the 1165 residue and dry with N₂. Figure 3.2(e)-(f) schematically show the results of this metal deposition before and after lift off.

 $^{^7\}mathrm{Microposit}$ photodeveloper, distributed by Microchem Corp., Westborough, MA http://www.microchem.com/



Figure 3.3. (111) Sample Schematic and Complete Sample Dimensions (a) Photograph of a completed a sample after the Lithography steps are complete. The sample is wire bonded with aluminum wires bonds to our homemade 32 pin header. The red scale bar shows serves as a size reference for the chips (b) False color SEM image of a single Hall bar. Each Hall bar device has 6 bonding pads with dimensions D1 \approx 200 μ m by 200 μ m; is a length of D2 \approx 1000 μ m; with a length of D4 600 μ m in between the longitudinal probes; and has a width D3 \approx 100 μ m.

After the above steps have been completed, the samples are ready for measurement provided the material characterization steps described later in this chapter have also been completed. I have included a sample schematic and SEM images of a completed sample in Figure 3.3(a) & (b), where both the LAO/STO Hall bar and metallized sections are visible. The SEM images showed that, even with careful lithography, there was always some mismatch not only between the metal contact pads and the Hall bars, but more importantly, between the transverse Hall voltage leads. This mismatch is due to the finite resolution of the photolithography process, and in the samples measured for this thesis ranged from 1-3 μ m, or about 0.16 - 0.5% of the longitudinal Hall bar length. As a final note, on all of the NUS samples I chose to use the MA/BA 6 mask aligner for the initial etch mask layer. This was done primarily because the MA/BA 6 alignment stage allowed for the alignment of the Hall bars along the sample chip edges to < 0.5°. This extra step is not entirely necessary as even in the flood exposure system careful alignment will yield an angular mismatch of 1 ~ 3 degrees.

If devices with a minimum feature size of $< 1 \ \mu m$ are desired, then electron beam lithography will be used to expose the device patterns. Recipes for the e-beam resist bilayers can be found in Appendix A.

3.1.2. Ar Ion Milling

In this section I will discuss the use of Ar ion milling, both to define the Hall bar devices, as well as make the surface of bare STO conducting. To start, I will briefly discuss the ion milling process, and then move to describing the procedure used for device definition. Finally, I will describe my work on the creation of process to make the surface of (111) STO substrates conducting.

3.1.2.1. Milling for Device Definition

Ar ion milling is a dry-etching process that has been widely used to define structures, not only in TMO materials, but also in conventional silicon electronics.¹³⁰ Ar ion milling has been found to have a number of advantages over chemical etching techniques, including lack of chemical contamination and less undercutting of the mask material due to the directed nature of the beam.

The Ar ion mill built by my fellow graduate student Varada Bal uses a Kaufman and Robinson KDC 40 DC gridded ion source⁸ to generate the ion beam used in the milling process. Figure 3.4 schematically shows how these DC gridded sources operate.¹³¹ First, Ar gas is injected into the discharge chamber (green port) where it is ionized by electrons emitted from a cathode filament (red). These Ar⁺ ions from a plasma which is accelerated by a negatively biased grid in the center of the ion source. Immediately down stream of the grid is a neutralizer filament, which emits electrons to neutralize the Ar⁺. If the neutralizer current is the same as the ion beam current the beam will be completely neutralized and the sample will be struck by neutral Ar atoms.¹³⁰



Figure 3.4. **DC Gridded Ion Mill**: Schematic of a DC gridded Ar ion beam source in a configuration similar to the one used in the Chandrasekhar group. Figure adapted from Ref. 131.

⁸http://ionsources.com

Parameters for etching ≈ 26 nm into the surface of the (111) LAO/STO heterostructures are given in Table 3.1. The parameters were developed in conjunction with Varada Bal and the engineers at Kaufman and Robinson to produce a stable ion beam. Crucially, these parameters will not cause the surface of the etched areas to become conducting, thus the four Hall devices on each sample are electrically isolated, with a device to device resistance exceeding 1 P Ω .

Parameter	Value
Ar pressure	1×10^{-3} Torr
Accelerating voltage	120 V
Accelerating current	5.2 mA
Beam voltage	600 V
Beam current	43.9mA
Discharge current	1.4 A
Discharge voltage	$40 \mathrm{V}$
Neutralizer current	13.1 A
Neutralizer voltage	11.5 V
Cathode filament current	8.04 A
Cathode filament voltage	10.6 V
Time	$3 \min$
blo 3.1 Etching parameters	for Ar jon milli

Table 3.1. Etching parameters for Ar ion milling.

3.1.2.2. Milling for Conduction

In addition to defining the Hall bar devices, it has also been shown by multiple groups that Ar ion milling could be used to make the surface of (001) STO conducting.^{132–135} They did this by exposing the samples to ion beams with much lower beam currents and accelerating voltages than used in the milling process. This ionic bombardment caused oxygen vacancies to build up at the surface, which gave rise to a 2DCG at the surface. I have conducted similar experiments on (111) STO substrates with both singly terminated surfaces, which exhibited good atomic steps, and unprocessed surfaces, which exhibited no atomic steps. I found that in on both surfaces cases I could indeed create a 2DCG.

In the first set of experiments I prepared a singly terminated (111) STO substrate using the procedures discussed in the introduction of Chapter 3. I also prepared another singly terminated (111) STO substrate using the following procedure modified from Ref. 110:

- (1) The sample was boiled in 18 MΩ D.I. water obtained from the Keck biophysics facility for 2 hours. This D.I. water etch removed any Sr compounds, but could not remove the Ti compounds.¹¹⁰
- (2) The sample was then annealed in the Chandrasekhar group's quartz tube furnace with 400 sccm of ultra high purity (UHP) O₂ flowing at 1000° C for 6 Hours.
- (3) The sample was boiled again for 2 more hours in 18 MΩ D.I. water to remove any Sr compounds that nucleate during the anneal.
- (4) Finally the sample was sonicated for 30 minutes in fresh 18 M Ω D.I. water.

Figure 3.5(a)/(b) shows that both the HF/D.I. water etching processes yielded clear atomic terraces; nonetheless, the surfaces on the D.I. water etch samples exhibited much more disordered terraces and obvious contamination. These surfaces could have been improved with further tuning of the D.I. water etch process. Indeed Chang *et al.* have shown that the D.I. water etched surfaces can be made to have morphologies identical to the HF surfaces; however, these singly terminated interfaces proved to be unimportant to the overall formation of a 2DCG. After the two singly terminated samples were fabricated, I exposed them, as well as a series of unetched samples, to a low energy ion beam with the



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Figure 3.5. **AFM Characterization of Two STO Etching Processes**: (a) 600 nm by 600 nm AFM image of STO samples subjected to the HF etching process. (b) 1.7 μ m by .7 μ m AFM image of STO samples subjected to the D.I. water etching process. Both images have the same height scale.

parameters given in the Table 3.2. I have made bold the parameters that were changed between the processes and seemed to most effect the conduction parameters.

Parameter	Value
Ar pressure	1×10^{-3} Torr
Accelerating current	3.1 mA
Accelerating voltage	60 V
Beam current	$12.9\mathrm{mA}$
Beam voltage	300 V
Discharge current	1.4 A
Discharge voltage	$40 \mathrm{V}$
Neutralizer current	11 A
Neutralizer voltage	$7.2 \mathrm{V}$
Cathode filament current	8.04 A
Cathode filament voltage	10.6 V
Time	$3 \min$
Table 3.2. Parameters for Ar	ion bombardment

The two singly terminated samples and an unprocessed sample were exposed to ion bombardment for 30 minutes, while the additional unetched samples were exposed for 40, 50, or 60 minutes. Figure 3.6 shows the sheet resistance (R_L) measured in the van der Pauw geometry as a function of bombardment time. All three sample types showed a similar $R_L \approx 172 \text{ k}\Omega$. As the bombardment times increased the unetched samples continued to decrease in resistance until 50 minutes, after which the resistance plateaued. I also tested the samples for conduction through the thickness of the substrate, finding that the bulk remained insulating even for the longest exposure times. These findings were in good agreement with the results of previous studies, which attributed this plateau to the point when the low power ion beam started etching away the top most STO layer.¹³⁵ Unfortunately, milling the samples with atomic terraces seems to damage/destroy the terraces. Thus I processed new (111) STO chips so that they would exhibit terraces and then subjected them to longer milling times, 40 and 50 minutes. Figure 3.6 shows that the STO samples with atomic terracing have the same surface resistance as the unetched samples.

This proof of concept experiment shows that ion milling can create a 2DCG in (111) STO and that this 2DCG need not be on singly terminated STO. Hopefully these results can be used by the next generation of students to expand our investigations to these nominally unstrained structures, and where the carriers at the interface would have only a single, well-defined origin, i.e. oxygen vacancies.



Figure 3.6. (R_L vs ion bombardment time for the unetched samples (black), D.I. water etched (red), and HF etched (green).

3.2. Materials Characterization

I will now move on to the materials characterization techniques that were utilized to determine the in-plane crystal directions, surface quality, and oxygen vacancy concentration. As my research is focused on the electronic transport characteristics of these heterostructures, I will only describe the essence of the techniques as well as their importance for later measurements.

3.2.1. X-Ray Characterization

The results I will describe later rely critically the identification of crystal directions, thus it was necessary to determine which in-plane direction each Hall bar device lies along. While traditional X-ray diffraction can be used to identify the in-plane crystal directions, characterizing the samples with the Photonic Science Laue camera in Northwestern's J.B. Cohen X-Ray Facility is far quicker.



Figure 3.7. Laue Diffraction: (a) Schematic representation of the Laue back reflection geometry used in the x-ray characterization. (b) Simulated Laue results along with the x-ray beam incident on the (111) plane. (c) Representative Laue back reflection data. Figure 3.7(a) is taken from Ref. 138

The Photonic Science Laue camera uses the so called backscatter geometry, shown schematically in Figure 3.7(a).¹³⁶ In this method a white continuous spectrum X-ray beam is incident on the (111) LAO/STO sample through the Laue camera along the [111] direction. The beam is then reflected off the sample and the reflections are recorded on 2D imaging plate placed a distance d away. For each crystal plane orientation, d and θ are fixed, and for any given n there will be some λ that satisfies the Bragg condition

$$(3.1) 2d\cos(\theta) = n\lambda,$$

producing a diffraction spot on the imaging plate at an angle 2θ with respect to the incident beam.¹³⁷ It is important to note that, due to the continuous spectrum of irradiation, n orders of interference will be super imposed on the same spot as a consequence of d and θ being fixed.¹³⁷ The sample is mounted on a precision goniometer with a 0.001° resolution, allowing us to carefully align the sample.¹³⁶ Figure 3.7(b) shows a Laue image take from a (111) LAO/STO sample that is slightly rotated in the (111) plane. This image is fit with the built in Photonic Science crystal orientation software which confirms the crystal orientation and in-plane crystal direction. This fitting can be confirmed by simulating the Laue response of (111) LAO/STO using a software like QLAUE. Figure 3.7(c) shows the results of one such simulation and when combined with the built in fitting software confirms that edges of the all of the samples align with the $[\bar{1}\bar{1}2]$ and $[1\bar{1}0]$ within 1°.

3.2.2. AFM Surface Characterization

Surface characterization of the (111) LAO/STO samples is extremely important for two reasons. First it confirms the epitaxial nature the LAO growth due to the existence of atomic terraces. As I discussed before, these terraces arise from the miscut in the STO substrate, causing a slope on the surface of the substrate.¹¹⁴ In general these are $< 0.5^{\circ}$ from the manufacturer, MTI corporation.⁹ The second reason for characterizing the surface of the (111) LAO/STO is to check the orientation of the terraces with respect to the Hall bar devices. The orientation of the atomic steps to the device is very important because as current moves along or transverse to the step edges, it can cause a large differences in device resistance on the same sample.¹⁰⁵ The Park XE150 AFM was used

⁹http://www.mtixtl.com



Figure 3.8. **AFM Characterization of (111)LAO/STO Samples**: (a) 6 μ m by 6 μ m AFM image of LAO/STO samples that exhibit no contact problems. (b) 6 μ m by 6 μ m AFM image of LAO/STO samples that rarely exhibit contact problems. (c) 6 mum by 6 μ m AFM image of LAO/STO samples where < 40% of the contacts do not show conduction. (d) 6 μ m by 6 μ m AFM image of newest LAO/STO samples, which show no steps what so ever.

in non-contact AFM mode to characterize the samples. Figure 3.8(a) shows an AFM image representative of the samples that were measured for the work I will present in the results section. I have marked Hall bar device directions in each image and for every sample measured the atomic terraces propagate at $45^{\circ} \pm 1^{\circ}$ to the Hall bar devices. Thus there should be no anisotropic contributions due to the terracing.

Unfortunately, some of the later (111) LAO/STO samples chips I received from NUS showed problems, namely these samples did not maintain sample conduction through all of the leads at low temperatures and at more negative V_g . More specifically, some Hall bar leads would become completely insulating, with resistances >> 1G Ω . Initially I thought this was a problem with the aluminum wire bonds losing conduction due to either disorder, Schottky barriers, or not punching through LAO film. However, after characterizing the surface of the samples, I found that the samples which showed a poor conduction also had poorly defined terraces. Figure 3.8(c) shows that these samples had far more jagged, irregular, terraces that were not periodic in any direction. In samples where > 75% of the leads showed no conduction at 77K, there were no visible atomic terraces. Figure 3.8(a) and (b) show AFM images of the highest quality samples that show good conduction and no contact issues. Figure 3.8(d) shows a sample from the newest batch of samples which shows no steps whatsoever.

Our collaborators are currently investigating the cause of this surface degradation, but the results show just how hard it is to achieve consistent termination at the (111) STO surface and how important it is to the quality of the conducting properties at the interface. These results are also relevant to any further experiments conducted on the Ar ion bombarded STO samples. While the all three sample surfaces (HF etched, D.I. water etched, and unetched samples) showed the same resistance at room temperature, the unetched samples may stop conducting at low temperature and more negative V_g .

3.2.3. Photoluminescence Measurements

Photoluminescence (PL) is defined as the emission of light from a material after the optical excitation, and PL spectroscopy is a powerful, nondestructive tool, for examining the optoelectronic properties of semiconducting materials.¹³⁹ In LAO/STO systems PL spectroscopy is particularly useful as it can be used to identify discrete electronic states that are not only intrinsic to the system, but can also identify transitions involving defect states at the interface. For the most part, these defect state transitions are due to oxygen vacancies at the interface. Thus, PL spectroscopy can be used to qualitatively confirm the existence and relative concentration of these vacancies.

Kan *et al.* were the first to report the existence of blue light emission from Ar ion bombarded STO.¹³³ Similar to the data I showed in the Section 3.1.2.2, this Ar ion bombardment caused the surfaces of the STO to become conductive. They used PL spectroscopy to investigate these conducting samples, and as Figure 3.9(a) shows, found that the irradiated samples showed a broad peak in PL response centered at $\approx 430 \text{ nm.}^{133}$ This peak did not shift in wavelength with increasing irradiation, and instead grew in amplitude. The inset of Figure 3.9(a) shows that this increase in peak amplitude began to saturate after 10 minutes of bombardment. This saturation was mirrored in the surface conductivity of Kan *et al.*'s samples and a similar effect was observed in my proof of concept tests.

Kan *et al.* also examined the PL response for crystalline (001) STO grown on (001) STO via in a low oxygen partial pressure (10^{-5} Torr) , and found that an identical peak existed in these samples.¹³³ This allowed them to identify oxygen vacancies as the culprit behind this emission. In Kan *et al.*'s model, presented if Figure 3.9(b), these vacancies

created defect levels in the STO band gap. Other researchers have preformed time resolved PL coupled with DFT calculations which confirmed that these oxygen defects create both acceptor and donor levels in the gap.^{?,140,141} At room temperature the lifetime of the electron in the defect states was short, and thus electrons excited to the Ti 3*d* conduction band rapidly recombined with the excited holes in the defects state. As oxygen vacancy concentration was increased, the number defect levels, as well as the number of electrons in the conduction band, rose, and consequently more recombination events occurred resulting in a larger peak height.¹³³



Figure 3.9. Energy Diagram of STO Photoluminescence: (a) Photoluminescence spectra of non-irradiated and Ar⁺-beam irradiated STO crystals. (b) The recombination process between the conduction electrons and the excited holes, which emits blue light at room temperature. Figure and caption adapted from Ref. 133



Figure 3.10. Photoluminescence response of As-Grown (111) LAO/STO heterostructures: Photoluminescence spectra of 20 UC (111) LAO/STO heterostructures grown in 1 mTorr of O_2 at 600°C. The spectra is taken after fabrication but without any post-growth annealing.

Kan *et al.*'s findings have been applied in a number of more recent publications to identify samples with oxygen vacancies.^{89,135} I have used the same PL spectroscopy technique to identify oxygen vacancy concentration differences in my as-grown and annealed samples. To conduct these experiments, I used the Stern group's IK Kimmon UV Laser, which emits 325 nm light to irradiate the sample while a Andor SR-303i Spectrometer was used to monitor the PL. The PL response measured for an as-grown sample is shown in Figure 3.10 and demonstrates that our samples also show a strong peak at 430 nm that is well above the background. While the peak for the as-grown samples was narrower than the peak seen by Kan *et al.*,¹³³ it matches fairly well the data seen in other groups.^{89,142} More interestingly there was a higher wavelength peak centered at 485 nm, that does not match any transitions investigated by Kan *et al.* or others. In the results chapter I will show that *both* peaks evolved with post-growth treatment, indicating that both peaks were tied to the oxygen vacancies that were present at the interface.

3.3. Electrical Measurement Techniques

In this section I will discuss the electrical transport and cryogenic techniques used to characterize the sample as a function of a wider variety of stimulus. All of these techniques have been utilized by the Chandrasekhar group over multiple generations of graduate students, and have been described in great detail in previous theses.^{119–124} Thus I will completely eschew a description of the cryogenic techniques and only focus on the electronic techniques and parameters that effect measurments of the (111) LAO/STO interface. These include the careful selection of ac excitation frequency and the slow drift that occurs at negative backgate voltage, V_g . I will additionally discuss the the technique I helped develop for measuring the AC capacitance over a large DC voltage range, and how we can apply it to measure the capacitance of the 2DCG. This capacitance is directly proportional to the density of states.

3.3.1. AC Differential Resistance Measurements and Parameters

The data that I will present later in the thesis is, for the most part, a measure of a change in resistance as a function of V_g , dc current, magnetic field, etc. In all of the resistance measurements presented, resistance is measured with a four probe technique utilizing a lock-in amplifier, homemade high impedance current source, and low noise voltage amplifier to measure the differential resistance, dV/dI. The explicit techniques

are discussed at length in previous theses,^{119–124} but in brief the measurement set up is as follows:

- (1) A lock in amplifier (LIA) (either the analog SR124/PAR124¹⁰ or digital EG&G 7260) supplies a voltage to the input of the current source at a frequency f_{LIA} .
- (2) The current source utilizes a AD624 instrumentation amplifier¹¹ referenced to an AD549 electrometer chip¹² to convert the lock in oscillator voltage to an ac current I_{ac} at f_{LIA} . The current source is also equipped with a sense resistor, which is used to both measure amplitude of I_{ac} and set the phase of the LIA to measure only the component of the sample response in phase with the current.
- (3) I_{ac} is then sourced through the sample to ground and the voltage across the sample is amplified by an instrumentation amplifier, in this case either an AD624 or INA110.¹³
- (4) Finally the amplified sample voltage is fed back into the LIA input which detects only the portion of the voltage at f_{LIA} .

While the experimental techniques that I use in my measurements have been developed and utilized by previous students, and even applied to (001) LAO/STO heterostructures, the (111) LAO/STO heterostructures present unique challenges to measurement. These challenges are twofold. The first arises from the extremely large resistances that can be achieved with application of negative V_g . The second challenge arises from a long time scale drift that is present at all V_g , but is greatly magnified at negative V_q .^{29–32}

¹⁰http://www.thinksrs.com/products/SR124.htm

¹¹Precision Instrumentation Amplifier AD624,' www.analog.com, (1999).

¹²Ultralow Input Bias Current Operational Amplifier AD549,' www.analog.com

¹³Fast-Settling FET-Input INSTRUMENTATION AMPLIFIER, INA 110,' www.ti.com, 2005.

The (111) LAO/STO heterostructures are far more resistive than their (001) LAO/STO brethren. For the as grown samples the longitudinal sheet resistance, R_L , can exceed 10 $M\Omega/\Box$, compared to 2.25 k Ω/\Box for the (001) LAO/STO samples. When in this high resistance state, the the sample rectifies I_{ac} into a large dc voltage. This dc voltage is not picked up by the lock-in, and if voltage becomes extremely large (≈ 10 V) the LIA input can overload. This can be seen most clearly by examining the black trace in Figure 3.11(a), which represents a measurement of R_L vs V_G at $f_{LIA} = 24.7$ Hz. The trace shows that at $V_g \approx -10$ V there is a turnover in R_L which is accompanied by a large 8 ~ 10 V DC voltage on the input of the LIA.



Figure 3.11. 111) LAO/STO Measurment Complications: Longitudinal sheet resistance as a function of V_g for two frequencies both taken at 4.4 K. (b) Hall resistance as a function of perpendicular magnetic field at $V_g = -10$ V at 4.4 K. Each 600 mT to -600 mT sweep takes 2 Hours.

This rectification can be avoided if a suitably low frequency is chosen for I_{ac} . The red trace in Figure 3.11(a) shows a measurement of R_L vs V_G at $f_{LIA} = 3.7$ Hz taken on the same Hall bar device on the same cool down and shows no turn over in R_L and a DC

voltage < 10 μ V. All of the measurements in the results section are taken with $f_{LIA} < 3$ Hz, thus avoiding the rectification.

The second complication that occurs in the (111) LAO/STO is a drift in R_L and the Hall resistance R_{XY} . This drift relaxes very slowly and has been observed in (001) LAO/STO heterostructures. Unfortunately in the (111) LAO/STO, especially at negative V_g and mK temperatures, this relaxation can occur over days, or even weeks. An example of this drift is shown in Figure 3.11(b) where the $R_{XY}(\mu_0 H = 0)$ drifts approximately 15 Ω over 8 hours. At this point in our work I have not found a way to circumvent or even mitigate this drift. The only solution is to wait until the drift relaxes and trace/re-trace occurs in the data. I should note that in the superconducting state this drift is completely non-existent, even when the sample is pushed into the normal state by I_{dc} . This glassiness may prove to be an interesting part of future studies.

3.3.2. Capacitance Measurements

While measurements of R_L and R_{XY} can give us a great deal of information about the properties of the (111) LAO/STO system, in many cases the results of these measurements are muddled by the complexity of the system. For instance, the Hall response is complicated by the fact that there are multiple bands, and even multiple carrier species, at the interface, making the process of extracting exact carrier densities and mobilities difficult if not impossible. In an effort to help circumvent this ambiguity I have measured the capacitance of a 2DCG system, thus gaining access to a quantity dubbed the quantum capacitance, which is directly related to the density of states (DOS). The use of capacitance to measure the DOS in low density materials 2D materials has its origin in the characterization of GaAs/AlGaAs heterostructures,^{97,98} and has been used in a host of systems, like graphene,¹⁴³ MoS₂,¹⁴⁴ and (001) LAO/STO.¹⁴⁵ To understand how the capacitance in these systems is different from that in a traditional metallic parallel plate capacitor, consider the schematic representation of a metal/insulator/graphene structure shown in Figure 3.12(a). At zero bias the Fermi levels in both the metal and graphene are the same. Once a potential, eV, is placed on structure, not only does the potential between the two electrodes, $e\phi$, shift, but the chemical potential in the graphene, μ , also shifts. Thus we can write down the total potential,

$$(3.2) eV = e\phi + \mu,$$

Then differentiating with respect to n, and rearranging the terms gives,

(3.3)
$$\frac{1}{C_{Tot}} = \frac{1}{C_{Geometric}} + \frac{1}{e^2 S \frac{\mathrm{d}n}{\mathrm{d}\mu}}$$

This last term is the quantum capacitance, $C_Q = \frac{e^2 S dn}{d\mu}$, and adds in series with the geometric capacitance. Provided the geometric capacitance does not change with the potential, measuring the capacitance of the system is a powerful method of determining the change in DOS.

However, before moving on, the careful reader may ask, why measure the DOS in a 2D material? After all it is constant. The answer to this question is simple, the DOS in a 2D material is only constant in the case of a parabolic, free electron, dispersion. Materials that deviate from this dispersion, like graphene, quantum hall insulators, topological

insulators, materials with negative compressibility, etc will exhibit an energy dependent DOS.



Figure 3.12. Capacitance Measurment Setup and Model: (a) Band schematic of a metal/insulator/graphene capacitor. Image adapted from 143 (b) Schematic of the capacitance measurement setup. The current pre-amplifier acts as a virtual ground connected to the 2DCG. (c) Model diagram of the measurement r_S corresponds to the sheet resistance per unit length of the 2DEG, c corresponds to capacitance per unit length, and g the conductance per unit length of the STO substrate. Figure (b) and (c) and associated caption adapted from Ref. 31

To measure the capacitance of the 2DCG, I helped develop a technique similar to the one used in the characterization of GaAs/AlGaAs heterostructures.^{97,98} Figure 3.12(b) shows a schematic representation of the setup, where an ac voltage excitation ($V_{ac} = 10 \sim 100 \text{ mV}$) from an EG&G 7260 LIA is superimposed with a ±10V DC excitation supplied by an Agilent/SRS signal generator via a home built summing amplifier.31 This summed signal is then amplified by a Kepco 100/1 power supply (gain of 10) and applied to the

backgate of the sample. A Hall bar device at the LAO/STO interface serves as the other electrode, and is connected to the inverting input of a homemade current pre-amplifier which acts as a virtual ground. The output of the current pre-amplifier is fed in to the input of the LIA where the in-phase and out of phase components of the signal applied to the backgate are simultaneously measured.

The simplest model that can be used to understand these signals places the system capacitance, C in parallel with a leakage resistor, R. The frequency dependent current i that passes through the amplifier from the sample is then given as,

(3.4)
$$i\cos(\omega t) = V_{ac}(\frac{1+j\omega RC}{R})\cos(\omega t).$$

For large R and ω the current through the sample is, $i \approx v j \omega C$, thus in this simple model the capacitance signal is the out-of-phase component. To be more explicit, the capacitance that is read off the LIA is,

(3.5)
$$C = \frac{1}{2\pi f} \frac{V_{LIA}}{V_{ac}} \frac{1}{\text{Gain}},$$

where f is the linear excitation frequency, V_{LIA} is the out-of-phase voltage measured by the lock-in, and 'Gain' is the voltage to current conversion factor of the current preamplifier, usually 10⁷ V/A. The excitation frequency was chosen to be as high as possible while still being in the flat frequency response regime of the Kepco 100/1, in the case of my measurements f = 2.3 kHz.³¹

However this simple model neglects the fact that the 2DCG may have large resistances at negative V_g . To determine if this in-plane resistance drastically effect the results of the measurement we have modeled the system as a transmission line. Figure 3.12(c) shows this model where c is the capacitance per unit length, c = C/L, g is the conductance per unit length, g = G/L between the backgate and the 2DCG, and r_s is the interface resistance per unit length, $r_s = R_s/L$.



Figure 3.13. Admittance and Capacitance Fits: (a)-(b)Imaginary and real components of the admittance as a function of the frequency $f = \omega/2\pi$ of the [110] Hall bar at 4.4 K, for $V_g = 0$ V. The black curves are fits to Eq. SB1 with parameters Rs = 25.4 k Ω/\Box , $G = 1 \times 10^{-15}$ S and C = 63.5 pF. (c) Solid symbols: Capacitance obtained by simultaneously fitting the real and imaginary components of the measured admittance to Eq. 3.7 at each value of V_g , for the [110] Hall bar device at 4.4 K. Solid lines are the measured quadrature component divided by ω . Figure and captions adapted from Davis *et al.*, Ref. 31.

This analysis leads to an admittance given by,³¹

(3.6)
$$Y = \frac{\sqrt{r_s(g+j\omega c)}}{r_s} \tanh(\sqrt{r_s(g+j\omega c)}L)$$
$$= \frac{\sqrt{R_s(G+j\omega C)}}{R_s} \tanh\sqrt{R_s(G+j\omega C)}.$$

The red traces in Figure 3.13(a) and (b) show the frequency dependence of the imaginary and real parts of the measured admittance for the $[1\bar{1}0]$ Hall bar at 4.4 K and $V_g = 0$ V. The two parts of measured admittance are fit simultaneously to Eq. 3.6 and produce
fairly good fits with values of $R_s = 25.4 \text{ k}\Omega/\Box$, $G = 1 \times 10^{-15} \text{ S}$ and C = 63.5 pF. The values of R_S and G agree well with the experimental values: R_s agrees with 10% of the measured resistance and value of G agrees with the measurement floor of the current pre-amp. In fact, the fits are completely insensitive to G over this range of frequency, thus from here on out we set G = 0. While there is a slight discrepancy between the fits and the data, the discrepancy has a very simple source, which is that the lock-in amplifier is fixed at a single phase while the Kepco's phase shift varies over the frequency range.

Nevertheless, in the limit of G = 0 we can analytically break up the real and imaginary parts of Eq. 3.6 into Y = Y' + jY'' where,

(3.7)
$$Y' = \frac{\sqrt{2\omega CR_s}}{2R_s} \frac{\sinh\sqrt{2\omega CR_s} - \sin\sqrt{2\omega CR_s}}{\cosh\sqrt{2\omega CR_s} + \cos\sqrt{2\omega CR_s}}$$
$$\frac{1}{2R_s} \frac{\sqrt{2\omega CR_s}}{\cosh\sqrt{2\omega CR_s} + \sin\sqrt{2\omega CR_s}}}{\cosh\sqrt{2\omega CR_s} + \cos\sqrt{2\omega CR_s}}$$

We used Eqs. 3.7 to simultaneously fit the measured real and imaginary admittance at f = 2.3kHz as a function of V_g , constrained to the measured R_s . Figure 3.13(c) shows the results of these fits compared to our simple model of Eq. 3.5, where the solid lines red lines are the measured C calculated from Eq. 3.5 and the black dots are from the fits to Eq. 3.7. Both models produce almost identical curves, showing that the 2DCG resistance does not affect the measured capacitance. Thus the imaginary component is simply $Y'' = \omega C$.

3.3.3. T_C vs $\mu_0 H$ and V_g Phase Diagrams

We have utilized a feedback method to continuously measure the T_C as a function $\mu_0 H$ and V_g . This feedback measurement has been covered in detail in Manan Mehta's thesis,¹²⁵ however a short description is as follows. We used an Adler-Jackson AC resistance bridge (see previous theses for the circuit diagram),¹¹⁹ and set the balance resistor, R_{bal} , to the value of the longitudinal resistance R_L at the superconducting transition temperature T_C , in this case defined as the mid-point transition between the resistive and superconducting state. The bridge produced a voltage proportional to the difference between the balance resistor and the sample resistance such that when $R_L = R_{bal}$, the output voltage was 0. This voltage was measured by an HP multimeter and feed into a proportional-integralderivative (PID) controller program written by Varada Bal in Lab-View, where the PID controlled the sample heater at the mixing chamber of the dilution refrigerator to maintain $R_L = R_{bal}$. The magnetic field or backgate voltage was then slowly swept and the PID changed the heater power, and thus sample temperature, to minimize the voltage from the bridge. The magnetic field or backgate voltage must be swept slowly enough for the sample temperature to equilibrate with the mixing chamber temperature. In all of the data I will present the curves completely traced and retraced provided the sweep rate was kept to < 25 μ Hz, requiring \geq 22 hours for a complete trace and retrace.

In the next chapter I will utilize these techniques to show that a surprising anisotropy exists in almost every single electronic property at the interface, this anisotropy is accompanied by the signature of hole carriers at the interface. The transport anisotropy appears below 22 K, providing tantalizing evidence of electronic nematicity.

CHAPTER 4

Results and Discussion

In this chapter, I will report on my results of the electrical transport measurements on (111) LAO/STO. The chapter is organized in the following manner: (a) first I will present a schematic of the sample geometry used in all of the samples; (b) I will then move on to describing the anisotropic longitudinal resistance, Hall coefficient, and capacitance of the samples above 4 K; (c) I will then discuss how these properties can be manipulated by post-growth treatments; (d) how this anisotropic behavior points to the existence of an electronic nematic state at the interface; (e) detail the behavior of the samples below 4 K starting with the superconducting state that nucleates at mK temperatures; (f)show evidence of the coexistence superconductivity and ferromagnetism seen in the hysteretic magnetoresistance; and (g) discuss the observation of a memory effect that occurs at mK temperatures.

As I reported in Chapter 3, all of the samples measured and reported on in this chapter were provided by Professors Venkatesan and Ariando's groups from the National University of Singapore. After the fabrication and characterization steps described in Chapter 3, the sample chips each had Hall bar devices patterned on their surface. The Hall bars were 1000 μ m long by 100 μ m, wide and the distance between the longitudinal voltage probes was 600 μ m. Figure 4.1 shows that for each sample chip, two of the Hall bar devices were fabricated along the [$\overline{112}$] direction and two were fabricated along the [110] direction. As a reminder, the [112] direction has a much larger overlap of the Ti t_{2g} bands than the [110] direction: this is shown schematically in the inset of Figure 4.1.

While I have measured 16 samples (64 different Hall bar devices) the data in this section of the thesis only reports on the 8 sample chips on which I have taken the most complete data. However, the other devices exhibited qualitatively and in some cases quantitatively similar results, even on devices that were grown by a different growth group. In addition, many of my more striking results have begun to be observed by other groups.^{39,147,148} For completeness and ease of reading I have included a table of all 8 samples from NUS. The remaining 8 sample chips were from a different research group and the data for those samples is not presented in this thesis, but reported qualitatively similar results. A table of these samples, their processing steps, and characteristics is given in Appendix B. In Table 4 each sample is labeled with a letter prefix (A,O,UV,H)#, where (A,O,UV,H) stands for the post-growth treatment type if any, and # stands for the sample chip number. When a sample chip undergoes a post-growth treatment the prefix changes but the number does not. Unless other noted all of the samples chips are grown as specified in Chapter 3.

To prepare for measurement the samples were electrically contacted via aluminum wirebonds using a Kulicke & Soffa Model 4123 ultrasonic wedge bonder.¹ The wire bonds mechanically punch through the LAO layer and form Ohmic bonds with the 2D carrier gas (2DCG). After the samples were wirebonded, they were placed in one of three cryostats: an Oxford Kelvinox MX100 dilution refrigerator, an Oxford Kelvinox 300 dilution refrigerator, or a home-built 1K insert. The as-grown samples chips all had longitudinal

¹www.kns.com

Sample Chip Number	Post Growth Treatment	Notes
A1	None	Later UV irradiated and
		subsequently relabeled UV1
A2	None	Later UV irradiated and
		subsequently relabeled UV2
A3	None	Later annealed in oxygen
		and subsequently relabeled
		03
A4	None	Later annealed in ar-
		gon/hydrogen environment
		and subsequently relabeled
		H4.
A5	None	Exhibited amorphous at-
		moic steps as seen in Figure
		3.8(c).
A6	None	Exhibited fairly good steps
		as seen in Figure 3.8(b)
A7	None	Dubbed the nematic sample
		in the text.
A8	None	Exhibited no atomic steps
		as seen in Figure 3.8(d), and
		very poor transport behav-
		ior
03	Oxygen annealed	Annealed 6 hours In O_2 at
		575° C. Then 45 minutes in
		an Ar/H_2 flow at 575° C.
UV1	UV irradiated	Irradiated for 15 minutes
UV2	UV irradiated	Irradiated for 7 minutes
H4	Ar/H_2 annealed	2.5 hours in an Ar/H ₂ flow
		at 575° C.

Table 4.1. Sample Numbers and Processing: The first column contains the sample chip numbers. The second column contains details on the post growth treatment conducted: none for the as-grown samples, oxygen annealed samples, UV irradiated samples, or Ar/H_2 annealed samples. Finally there is a column with notes on each sample. These notes are only for quick referencing and more complete descriptions are given in the main text.

resistances (R_L) of $\approx 23 \text{ k}\Omega/\Box$ at room temperature in all four Hall bar devices on each chip at an electrostatic backgate voltage, $V_g = 0$. This is expected, as the resistivity



Figure 4.1. **Sample Schematic**: Schematic representation of the surface of the (111) LAO/STO sample chip, showing the four Hall bars. The electrical connections for longitudinal and Hall resistance measurements used for the two Hall bars that are discussed in detail in the text are as marked. Also shown are the crystal directions determined from x-ray measurements. The inset shows a schematic representation of the Ti d_{xy} , d_{yz} and d_{xz} orbitals in a cubic crystal viewed along the [111] direction. Figure and captions adapted from Davis *et al.*, Ref. 31.

tensor for this interface was isotropic in the plane of the interface. R_L was measured on each device on the chip by the AC lock-in technique described briefly in Chapter 3 and in other theses. Schematically this technique measured R_L by sending an AC current from the inner "current" lead at the end of the Hall bar device to the outer "current" lead and then measuring the resulting voltage V_L .

The next step in the measurement process was to cool the sample chip to be measured to ≈ 77 K by placing the insert in a liquid nitrogen bath. In my measurements, all of the samples were *always* cooled to 77 K at $V_g = 0$ V and, after cooling, showed a resistance of $\approx 10 \text{ k}\Omega/\Box$ at 77 K. This cooling procedure maybe extremely important as any potential applied to the backgate at this point would create a symmetry breaking electric field on the 2DCG as it is cooled through the STO tetragonal structural transition temperature. The exact dependence of the electronic properties on field cooling may prove to be an interesting avenue for future research. Figure 4.2 shows that at 77 K, the R_L vs V_g traces for sample A1 were isotropic with respect to the in-plane crystal directions. Indeed all of the samples, regardless of post growth treatment, displayed isotropic R_L vs V_g dependencies at 77 K, which showed that the cubic to tetragonal structural transition of the STO substrate is not the source of anisotropy that we observed at lower temperatures.



Figure 4.2. 77K Longitudinal Resistance vs Backgate Voltage Dependence of Sample A1: R_L vs V_g at T = 77 K for sample A1. The black trace corresponds to the $[1\bar{1}0]$ direction and red trace to the $[\bar{1}12]$ direction.

4.1. Measurements for $T \geq 4\ K$

Once the samples were checked at 77K for good conduction through all of the leads, they were cooled to liquid helium temperatures, $T \sim 4.4$ K. This section is dedicated to the properties of the samples at these temperatures. The first two subsections will detail the surprising anisotropy that we observed in all of the electrical transport properties at the (111) LAO/STO interface, and how we tuned this anisotropy with post growth treatment. In the last subsection, I will report on the temperature dependence of these anisotropic properties and describe how this dependence points to the existence of an electronic nematic state at the interface.

4.1.1. In-plane Anisotropy

While all four Hall bar devices on each (111) LAO/STO sample had the same R_L at room and liquid nitrogen temperatures, at ~ 4.4 K the R_L of the devices in the [110] direction were nearly twice as large as the R_L of devices along the [112] direction at $V_g = 0.^{31,32}$. This was extremely surprising as the crystal symmetry of the interface implied that R_L should have been isotropic.^{31,32,100,101} This anisotropy was made even more striking by measuring R_L as a function of V_g . An example of this response is shown for sample A1 in Figure 4.3(a) where the black/(red) trace corresponds to continuous traces of R_L vs V_g along the [110]/([112]) direction.^{31,32} Interestingly, both traces were extremely hysteretic:³¹ that is R_L was higher when V_g was swept from -60 V \rightarrow 80 V than when V_g was swept from 80 V \rightarrow -60 V. For all samples the up-sweeps and down-sweeps always reproduced themselves, provided the sweep range and rate were kept constant.³¹

We also observed in all samples that if the sweep rate was slowed the hysteresis loop narrowed.³¹ Figure 4.3(b) shows this plainly for sample A1, where a 24 hour upseep/downsweep trace in blue was narrower than a up-sweep/down-sweep trace taken over 16 hours in black; however, while the up-sweeps and down-sweeps were different, the averages of the respective curves were identical.³¹ In fact, when we stopped sweeping the gate voltage the resistance immediately started drifting to the average R_L . This hysteresis was seen in all samples, is likely tied to glassy defect states at the interface, and has been seen in other LAO/STO heterostructures,^{20,23,23,31,32} and LSAT/STO heterostructures,¹⁴⁷ and is likely related to the drift in Hall resistance that I described in Chapter 3. While interesting, this hysteresis and drift are beyond the scope of my research; thus, for the remainder of Chapter 4 I will report the average of the up and down-sweeps, or in the case of the subsequent Hall data, after the sample has relaxed, so such averaging was not required.



Figure 4.3. As-grown Sample A1 Gate Sweeps: (a) Longitudinal sheet resistance R_L of the [110] and [112] direction Hall bars as a function of the back gate voltage V_g . The sweep direction is marked by arrows. The green and blue curves show the average of the up and down sweeps for the two samples. (b) Logarithmic plot of R_L vs V_g at two different sweep rates for the [110] sample. The black/(blue) curve corresponds to a 16/(24) hour long sweep of the back gate with its averaged curve in green/(red). The data was taken on sample A1 taken at 4.4 K. Figure and captions adapted from Davis *et al.*, Ref. 31.

Returning to Figure 4.3(a), the blue and green curves represent the averaged R_L vs V_g response for sample A1, measured for $[1\bar{1}0]$ and $[\bar{1}12]$ directions, respectively. When V_g was positive, R_L reduced to $\approx 100\Omega/\Box$, and the anisotropy was non existent. On the other hand, when V_g is negative, R_L grew to ≈ 180 and $42 \text{ k}\Omega/\Box$ for the $[1\bar{1}0]$ and $[\bar{1}\bar{1}2]$ directions respectively, and the anisotropy grew much larger than at positive V_g by nearly a factor of seven.³¹ This anisotropy is larger than the anisotropy seen in many other transition metal oxide materials¹⁵⁰ and iron-based semiconductors.³⁴⁻³⁶ Again, we observed this behavior was seen on numerous as-grown samples (A1,A2,A3,A4,A7) and was not effected by cycling through the 105 K structural transition of STO.^{31,32} This implied that the anisotropy was not caused by the tetragonal structure or by ferroelectric domain walls, which randomly reorient with temperature cycling.^{31,75,76} Furthermore, recall that all of the Hall bar devices were oriented at 45° to the atomic terraces due to the STO miscut, which means that the anisotropy could not be due to the terracing effects discussed in Chapter 3.^{31,105}

In order to get a better idea of the nature of the 2DCG and possibly the anisotropy, we measured the Hall resistance (R_{XY}) as a function of out-of-plane magnetic field, $\mu_0 H_{\perp}$.^{31,32} To do this, we again sourced an AC current from the inner "current" leads to the outer leads, but this time measured the resulting transverse voltage V_{XY} as a function of $\mu_0 H_{\perp}$. In all of the Hall measurements, there was a small offset in R_{XY} at $\mu_0 H_{\perp} = 0$ mT that was due to a 1 ~ 3 μ m mismatch in the transverse voltage leads. This offset is clearly seen for sample A2 in Figure 3.11(b) and complicates any analysis of the Hall response; however, R_{XY} was found to be linear in field and its slope electron-like out to ± 600 mT at 4.4 K for all V_g and for all samples chips, regardless of post growth treatment.

The slope of R_{XY} vs $\mu_0 H_{\perp}$ is defined as the Hall coefficient R_H , and for a single band material $R_H = \frac{1}{nq}$, where n is the areal carrier density and q is the unit of charge $\pm e$ for holes and electrons, respectively.^{31,32,102} Figure 4.4 shows the Hall coefficient $-R_H$ vs V_g for sample A1 where the black/(red) symbols represent R_H for the Hall bar devices along the [110]/([112]) direction and the negative sign comes from the electron like nature of the carriers.^{31,32} Mirroring the response in R_L , R_H for sample A1 was also anisotropic, where for Hall bar devices along the [110] direction, R_H exhibited a sharp rise in magnitude at $V_g \approx 20$ V, while for Hall bar devices along the $[\bar{1}\bar{1}2]$ direction, R_H gradually increased starting at $V_g \approx -30$ V. Above $V_g = 30$ V, both curves saturated to $R_H \approx 40\Omega/T$.³¹ This dependence is unexpected for a single electron-like carrier material. As V_g is increased, it is expected that electrons would be drawn to the interface, increasing the electron density n_e , and subsequently decreasing; $|R_H|$,³¹ instead we observed an increase in $|R_H|$ with V_g in both directions.³¹ Similar dependencies have been observed in (001) LAO/STO heterostructures, there the dependencies were explained via the existence of multiple electron bands with different mobilities.^{13,16,20,23} Our results can also be explained via multiple carrier bands, but at least one of these bands must correspond to a hole-like carrier.

We modeled this dependence of R_H on V_g with a simple two band model: one electron band and one hole band. R_H in this model was,^{31,32,102}

(4.1)
$$R_H = \frac{R_e \sigma_e^2 + R_h \sigma_h^2}{(\sigma_e + \sigma_h)^2},$$

where $R_{(e,h)} = \pm 1/(n_{(e,h)}e)$ are the Hall coefficients and $\sigma_{(e,h)} = n_{(e,h)}e\mu_{(e,h)}$ are the conductivities of the electrons and holes, respectively. Here, $n_{(e,h)}$ and $\mu_{(e,h)}$ were the



Figure 4.4. As-grown Sample Hall Coefficient as a Function of Backgate: Symbols, measured Hall coefficient R_H of V_g for the two crystal direction on sample A1; solid lines are fits to the two-band model described in the text. All measurements were performed on sample A1 at 4.4 K. Figure and captions adapted from Davis *et al.*, Ref. 31

corresponding areal densities and mobilities.³¹ To add a V_g dependence to R_H , we assumed that n_e and n_h had a simple linear dependence on V_g , and further simplified the model by assuming that μ_e and μ_h were independent of V_g .³¹ This gave us six parameters with which to fit R_H as a function of V_g : n_e ; n_h at $V_g = 0$ V; the linear slopes dn_e/dV_g ; and dn_h/dV_g , and the mobilities μ_e and μ_h . We used the measured R_L vs V_g data to reduce the number of parameters to 5, as $\sigma_e + \sigma_h = \sigma$, $\sigma = 1/R_L$.³¹ More specifically, we constrained $\sigma(V_g) = n_e(V_g)e\mu_e + n_h(V_g)e\mu_h$. The resulting fits are shown as solid lines in Figure 4.4 and in general showed a total carrier density $n = 10^{13}$ cm⁻² and a ratio of $n_e/n_h = 50$ for the [110] direction and 100 in [112] direction. However, as we were only fitting two data points per value of V_g and had 5 parameters there was a large range of values that would produce fits to the data. Regardless, the one constant in all the fits was that the drop in R_H at negative V_g could not be produced in the fits without a hole like carrier.

Returning to the anisotropy, if R_H was a direct measure of only the charge density n, as it is in single carrier materials, then the anisotropy would completely unexpected.^{31,99,102,146} In the multiband picture, however, R_H is a function of $n_{e,h}$ for each band as well as the $\mu_{e,h}$ for each band. Since R_L was different along the two directions for $V_g \leq 40$ V the mobilities along the two directions were also likely different; and thus this anisotropy may not be quite as surprising as it was at first glance. In an attempt to get a better idea of the nature of this anisotropy, we measured the capacitance of the system as described in Chapter 3.

In low-density 2DCGs, the capacitance (C) is the series combination of the geometric capacitance C_g and the quantum capacitance $C_Q = e^2 S \frac{dn}{dE}$,^{31,97,98,143–145} where S is the area of the 2DCG and $\frac{dn}{dE}$ is the density of states. All of the samples measured in this thesis had control devices fabricated locally on the bare STO.³¹ The control devices were Au pads deposited on bare STO and had no 2DCG underneath the top pad. These devices were used to calibrate C_g and ensured any effects we observed in the Hall bar devices were only due to changes in the 2DCG.³¹ Figure 4.5(a) shows the results of the capacitance measured on the control device on sample A2. Using the known control device area and the measured capacitance, we found the dielectric constant for all samples matched the bulk



Figure 4.5. Hall Bar Capacitance and Control Sample Capacitance for Sample A2: (a)Capacitance of control device, fabricated on chip with the hall bars, as a function of V_g , at 4.4 K. All measurements were performed on sample A2 at 4.4 K. (b) Averaged measured capacitance of the two Hall bars. Figure and captions adapted from Davis *et al.*, Ref. 31

measurements of STO $\approx 2.3 \times 10^{5.31}$ More importantly, this data in Figure 4.5(a) showed that the capacitance of the control device on sample A2 varied less than 1 part in 10^{5} over the entire V_g range.³¹ Thus, any change in the capacitance of the 2DCG was nominally due to a change in the quantum capacitance of the 2DCG. Additionally, the lack of any strong change in C_g showed that the dielectric constant of the STO was not suppressed by an electric field, which confirms my prior claim from Chapter 2 that we apply fields that do not suppress the quantum paraelectric phase of the STO substrate.^{31,41,65}

Figure 4.5(b) shows the average capacitance in black/(red) measured on sample A2 for the $[1\overline{1}0]/([\overline{1}\overline{1}2])$ direction. Unfortunately, we could not determine the absolute area of the Hall bar devices, because when the wirebonds punched through to the interface they decreased the effective area of the 2DCG capacitor; thus, direct, quantitative comparisons of *C* between devices was not possible.³¹ However, when we scaled the two curves so that

they matched at positive V_g , where the other electronic properties were isotropic, we found that C in both directions almost perfectly matched each other for $V_g \ge 20$ V.³¹ On the other hand, when $V_g \le 20V$, C for Hall bar devices along the $[\bar{1}\bar{1}2]$ direction decreased precipitously when compared to the Hall bar devices along the $[\bar{1}\bar{1}2]$ direction. This anisotropy was completely unexpected if we are measuring only changes due to the quantum capacitance, as the quantum capacitance and thus the density of states, dn/dE, is explicitly averaged over the Fermi surface. Near $V_g = 60$ V, C for both Hall bars began to saturate, however, the Hall bar devices along $[1\bar{1}0]$ direction showed a hint of an upturn in C at $V_g \le 70$ V.³¹ This upturn is not expected for a purely electron like material in which dn/dE would see a monotonic decrease in C with decreasing V_g and served as further evidence of a hole like carrier at the interface.^{31,143,145}

In this section, I have described how every electronic property of the 2DCG was found to be anisotropic at $T \sim 4.4K$, but I have not discussed the origin of these effects. Furthermore, as I described in Chapter 2, the 2DCG at LAO/STO interfaces can for through a range of mechanisms show anisotropic behavior, but I have not described or speculated as to which of these mechanisms, if any, gives rise to the anisotropy in these (111) LAO/STO heterostructures. In the next section, I will describe how we leveraged oxygen vacancies to investigate where this anisotropy "lived" at the interface and how changing the oxygen vacancy concentration can globally tune the anisotropy.

4.1.2. Tuning the Anisotropy with Post-growth Treatment

As I have established in Chapter 2 and 3, oxygen vacancies in STO are associated with defect states introduced into the band gap of the STO, which give rise to donor levels near

the STO conduction band edge and acceptor levels near the valence band edge. Each oxygen vacancy donates $2e^-$ to the 2DCG.^{133,142} These oxygen vacancies can be introduced to LAO/STO heterostructures during growth or through post growth treatment and are found to strongly affect not only the conductivity at the interface, but also magnetism and superconductivity.^{2,32,77–79,87,89–92} In this section, I will describe how we used postgrowth treatments to manipulate the oxygen vacancies at the (111) LAO/STO interface, and the effect this manipulation had on the anisotropy I discussed in the previous section.

We used three methods to manipulate the oxygen vacancy concentration at the interface: annealing in ultra high purity (UHP) oxygen gas, annealing in a 3:1 mixture of UHP Ar and H₂ gas, and irradiation of the samples via UV radiation.^{31,32} All of the samples used in this section were first characterized in their as-grown forms (samples A1, A2, A3, and A4) and exhibited qualitatively and quantitatively similar behavior. For the data presented in this section we subjected two as-grown samples to post-growth annealing in a quartz tube furnace.

Sample A3 was annealed in O₂ gas with a flow rate of 300 sccm for 6 hours at 575°C.³² The temperature was chosen to avoid melting the aluminum wire bond remnants which have melting temperatures of 625°C, while the flow rate was chosen based on the oxygen annealing flow rate used for STO substrate preparation. After 6 hours of annealing the samples were completely insulating, $R_L > 10^{12} \Omega$.³² Subsequently, the samples were annealed for 45 minutes in an Ar/H₂ flow (300 sccm:100 sccm) at 575°C³² to reintroduce oxygen vacancies to the interface, which enabled us to measure the samples.³² These annealing parameters were chosen as they produced a interface with higher R_L than the as-grown samples and were developed using sacrificial samples grown by a different group. Going forward I will refer to this sample as O3, and generally, samples like it as " O_2 " annealed samples.

Sample A4 was annealed in an Ar/H₂ flow (300 sccm:100 sccm) at 575°C for 2.5 hours.³² This greatly reduced R_L , but did not electrically short the 4 Hall bar devices to each other or the back gate.³² Hereafter I will refer to this sample as H4, and generally, samples like it as the "Ar/H₂" annealed samples. It is important to note that we can turn the O₂ annealed samples into Ar/H₂ annealed samples and vice versa simply by annealing with the appropriate gas mixture, and the samples will show the same properties provided the room temperature R_L 's match.³² Specifically, the O₂ annealed samples can be turned in to Ar/H₂ annealed samples by annealing the O₂ annealed samples in an Ar/H₂ flow (300 sccm) at 575° C for 4 hours. On the other hand, the Ar/H₂ annealed samples in an O₂ flow (300 sccm) at 575° C for 2.25 hours.

The last post-growth treatment used to modify the 2DCG characteristics was irradiation of samples A1 and A2 under UV light. UV irradiation was used by McKeown-Walker *et al.*²⁷ to induce oxygen vacancies at the surface, thereby increasing the carrier density. However, I will show that in our results this UV irradiation actually decreased the oxygen vacancy concentration at the interface. The difference comes from the fact that in McKeown-Walker *et al.*'s²⁷ case the UV irradiation occured in high vacuum, and the UV served to liberate oxygen from the interface.²⁷ In our case we irradiated the samples in ambient atmosphere at room temperature with a UV lamp designed to produce large quantities of ozone.^{31,32} The bulb we used was a Light Tech G36T5VH,² and it produces

²https://www.light-sources.com

UV light primarily at 185 nm and 254 nm, with a radiant flux of 17mW/cm^2 , and generates ozone at a rate of 1.8g ozone/Hour per the manufacture's specs. In our experiments we irradiated sample A1 for 15 minutes and sample A2 for 7 minutes, with the samples 1 mm away from the UV source. These sample chips are subsequently labeled as UV1 and UV2, respectively.^{31,32} This UV irradiation led to an increase in R_L from 22 k Ω/\Box to 34 k Ω/\Box for UV1 and from 22 k Ω/\Box to 27 k Ω/\Box for UV2.^{31,32} Throughout the process we monitored the temperature of the sample mount with a K-type thermocouple and found that the samples heated to at most 82°C, which implied that any changes in the sample properties were due to a chemical/structural change in the sample and not thermal annealing. However, we can rule out structural changes as the change in R_L reversed within a day, unless the sample was cooled to LN2 temperatures.^{31,32}

As I briefly discussed in the last few paragraphs, the first major effect of these postgrowth treatments is to change the room temperature R_L :^{31,32} in the as-grown samples, (A3, A1) R_L increases from $R_L \approx 22 \text{ k}\Omega/\Box$ to $R_L \approx 52/(34) \text{ k}\Omega/\Box$ for the samples O3 and UV1, respectively.^{31,32} On the other hand, the resistance Ar/H₂ annealed samples H4 reduced to $R_L \approx 17 \text{ k}\Omega/\Box$.³² The change in R_L was a strong indicator of a change in oxygen vacancy concentrations, where the O₂/(Ar/H₂) annealed samples would have fewer/(more) oxygen vacancies, and was in good agreement with previous findings of other groups.^{89,89,133,142} The UV samples (UV1,UV2) posed a more complicated situation, as at first glance their increased R_L seemed to run counter to the previously reported increase in oxygen vacancy concentration with UV radiation.^{27,31,32} However, with the differences in UV irradiation process described above it was reasonable to ascribe this increased R_L to a decrease in oxygen vacancies.^{31,32}



Figure 4.6. Photoluminescence as a Function of Post Growth Treatment: Room temperature photoluminescence intensity as a function of wavelength measured for the devices after various surface treatments. The gold, red, black, and blue curves correspond to the Ar/H_2 annealed, as-grown, 15-minute UV irradiated, and O₂ annealed samples: samples H4,A1,UV1,O3 respectively. Figure and captions adapted from Davis *et al.*, Ref. 32

We used the photoluminescence (PL) technique described in Chapter three to confirm these observations. The results of the PL studies are shown in Figure 4.6 where the response from the as-grown sample A2 is shown in red, with a prominent peak at ≈ 434 nm that was indicative of the oxygen vacancy concentration in the sample.^{32,133,142} The Ar/H₂ samples H4 showed a marked increase in this peak amplitude,³² indicating an increased concentration of oxygen vacancies,^{32, 133, 142} which agrees with the lower, room temperature R_L .³² Conversely, both the O₂ and the UV irradiated samples (O3,UV1) showed a 434 nm peak with decreased amplitude indicating a lower concentration of vacancies were present.^{32, 133, 142} These findings also confirmed that the increase observed in R_L for the UV irradiated samples (UV1,UV2) was due to oxygen vacancies.³²



Figure 4.7. R_L vs V_g After Post Growth Treatment: (a) R_L vs V_g for the as-grown devices A2. The data for the $[1\bar{1}0]$ direction are in black while the data for the $[\bar{1}\bar{1}2]$ direction are in red. The solid lines designate the average of the up and down sweeps shown in dotted lines for each direction respectively. (b)-(e) Average traces for both crystal directions after, O₂ annealing (sample O3), (b) Ar/H₂ annealing (sample H4), (c) 7 minute UV irradiation (sample UV2), (d) and 15 minute UV irradiation (sample UV1)(e). (f) The ratio $r_{aniso} = \frac{[1\bar{1}0]}{[1\bar{1}2]}$ as a function of V_g for each surface treatment. All data are taken at 4.4 K. Figure and captions adapted from Davis *et al.*, Ref. 32.

After post growth treatment, we cooled the samples back down to ≈ 4.4 K and examined the affects of the post-growth treatment on the anisotropic transport at the interface, starting with the response measured in R_L vs V_g . Figure 4.7(b) shows the averaged response in the O₂ annealed samples O3. It is immediately apparent that these samples have a much higher R_L at low back gate voltages than the as-grown sample A2 shown in Figure 4.7(a):³² for example, at $V_g = -20V$ the resistance in the Hall bar devices along the $[1\bar{1}0]/([\bar{1}\bar{1}2])$ direction was $\approx 200/(50)$ k Ω/\Box for the O₂ annealed sample O3,³² compared to a more modest $\approx 50/(15)$ k Ω/\Box for the as-grown sample A2.³² The fact that we found the O₂ annealed sample O3 to be much more resistive over nearly the entire range of V_g was expected based on the role of oxygen vacancies at the interface.^{2,32,77-79,87,89-92} Figures 4.7(d)-(e) show that similar to the O₂ annealed sample O3,³² data measured on the 7 min and 15 min UV irradiated samples (UV2 and UV1), which showed decreased oxygen vacancy concentrations, also showed increased R_L , especially at $V_g < 20$ V.³² On the other hand, the Ar/H₂ annealed sample H4 was distinctly less resistive than the as-grown sample A2, by almost an order of magnitude.³²

Surprisingly, the change in oxygen vacancy concentration induced by post-growth treatment had a dramatic effect on the anisotropy at the interface.³² Figure 4.8 shows a quantitative measure of this anisotropy, $r_{aniso} = R_{[1\bar{1}0]}/R_{[\bar{1}\bar{1}2]}$ as a function of V_g for each post growth treatment. The as-grown sample A2 was isotropic at highest positive V_g and gradually became more anisotropic at low negative V_g , up to a maximum factor of 6.³² The O₂ annealed sample O3 showed a similar increase in r_{aniso} with decreasing V_g , but the overall magnitude of r_{aniso} was much larger over the entire range of V_g .³² The UV irradiated samples (UV1 and UV2), on the other hand, showed a more complex change



Figure 4.8. r_{aniso} vs V_g After Post Growth Treatment: The ratio $r_{aniso} = \frac{[1\bar{1}0]}{[1\bar{1}2]}$ as a function of V_g for each surface treatment. Red corresponds to the as-grown sample A2, blue to the O₂ annealed sample O3, green to the 7 minute UV irradiated sample UV2, black to the 15 minute UV irradiated sample UV1, and gold to the Ar/H₂ annealed sample H4. All data are taken at 4.4 K. Figure and captions adapted from Davis *et al.*, Ref. 32

in anisotropy: where at high positive V_g the UV irradiated samples had a lower r_{aniso} than the as-grown samples. At low negative V_g the UV irradiated samples were more anisotropic than even the O₂ annealed sample despite the fact that they had lower R_L .³² Finally, the Ar/H₂ annealed sample H4 showed a radical departure from the as-grown samples with an r_{aniso} that was greater than 1, but nearly constant over the entire V_g range.



Figure 4.9.

 R_H vs V_g After Post Growth Treatment: (a)Hall coefficient, R_H , vs V_g for [110] oriented Hall bars for the devices measured after each surface treatment. (b) Corresponding Hall coefficient, R_H , vs V_g for Hall bars in the [112] direction for each surface treatment. R_H , vs V_g for the [110] direction in black and the [112] direction in red; for the (c) O₂ annealed O3, (d) as-grown A2, and (e) Ar/H₂ annealed H4 samples. All data taken at 4.4 K. Figure and captions adapted from Davis *et al.*, Ref. 31

While it was possible to draw some conclusions as to the nature of these anisotropic states from the data already presented; it is pertinent to examine the effect of the postgrowth treatment on the Hall response of the system, which gives additional information about the nature of the change in charge carriers at the interface. Figures 4.9 (a)&(b) show the measured R_H as a function of V_g for devices along the [110] and [112] directions respectively for the various post growth treatments.³² For both directions, removing oxygen vacancies from the sample via caused R_H to decrease precipitously at negative V_g ; however, the devices along the [1 $\overline{10}$] direction showed a much stronger response,³² reducing to $R_H \approx 0 \ \Omega/\text{T}$ for the O₂ annealed samples, with R_H beginning to drop at $V_g \approx 20$ V. Mirroring the changes seen in R_L , the Ar/H₂ sample H4 showed much less change in R_H as a function of V_g ,³² and did *not* show any sort of drop off at in either direction.³² The UV annealed samples continued to show a mixed response.³² In the [1 $\overline{10}$] direction the UV annealed samples UV1 and UV2 acted like O₂ annealed sample O3, with R_H exhibiting a sharp drop at $V_g \approx 20$ V; however, for the [$\overline{112}$] direction they showed little to no change from the as-grown sample A1.³²

This mixed response may be indicative of a more complicated thickness dependent change in the oxygen vacancy concentration, and deserves further investigation in future experiments.³² For now, I would like to take a closer look at the effects that the post-growth treatments have on the anisotropy in R_H between the two in-plane crystal directions. Figure 4.9(c)-(e) shows R_H measured for both the [110] and [112] directions as a function of V_g for the O₂ annealed O3, as-grown A2, and Ar/H₂ annealed H4 samples. Recast in this manner, the data clearly showed that the O₂ annealed sample (O2) was much more anisotropic than the as-grown sample A2 at negative V_g , while the Ar/H₂ sample H4 showed no anisotropy whatsoever. This dependence of the anisotropy in R_L and R_H on post growth treatmen leads to a model to explain the charge transport in-terms of three types of states:³² the intrinsic Ti t_{2g} orbitals that form the intrinsic bands in the STO, the states due to oxygen vacancy defects that exist just below the conduction band edge, and hole-like acceptor levels that lie just above the valence band edge.³²

The first type of state is due to the Ti $d_{xy,xz,yz}$ orbitals in the STO, which have C_3 symmetry at the interface.^{26,27,31,32} While the band overlaps are smaller in the $[1\bar{1}0]$ direction than in the $[\bar{1}\bar{1}2]$ directions,^{26,27} for both the cubic and tetragonal STO crystal structures, the conductivity should be isotropic simply based on the symmetry of the structures.^{99,100,102,146} However, our data suggested that the band edge in the $[1\overline{10}]$ is actually higher in energy than the $[1\overline{12}]$ direction. The second set of states that contribute to transport at the interface are the oxygen vacancies, which produce donor states below the conduction edge.^{133,142} The data show that when the samples have large oxygen vacancy concentrations,³² they displayed little to no anisotropy in either R_L or R_H . Conversely, when there samples have few oxygen vacancies, the anisotropy is extremely large. The third type of state is due to the small concentration of holes at the interface. As I discussed in subsection 4.1.1, our fits to the Hall coefficient suggest that these hole like states have a contribution to the carrier density that is at least three orders of magnitude smaller than the previous two electron-like states; however, due to the large uncertainty in our actual fit parameters we only know for certain that they exist, we do not know the overall magnitude of their carrier density.^{31,32}

All three types of states contribute to transport in the system with weights that depend strongly on the post growth treatment.^{31,32} At one extreme the Ar/H₂ sample H4 have a large number of oxygen vacancies which can have two effects. First, if the energy difference between the donor level and the bottom of the conduction band is less than k_BT (i.e. $-\epsilon_d - \epsilon_c | < k_BT$) then the oxygen vacancies donate electrons to the conduction bands. These donated electrons would suppress any anisotropy in the system as the Fermi level would be well above both band edges corresponding to the same situation as in high positive V_g .^{133,142} Second the oxygen vacancies create defect states in the system, which may form a continuous isotropic defect band in the system at high concentrations. In this case, even if the energy difference $|\epsilon_d - \epsilon_c| > k_B T$, the overlap between wave functions at different impurity sites may be large enough that conduction through the isotropic impurity band is still possible; thus eliminating any anisotropy in R_L or R_H .^{31,32,133,142} At the other end of the spectrum are the O₂ annealed sample O3, where the intrinsic bands provide the dominant contribution to electrical transport;^{31,32} that is until these bands are depleted with via application of a negative V_g . This implies that anisotropy in the system stems from the bands that are intrinsic to the interface, despite the fact that these bands should be isotropic.^{31,32} This breaking of in-plane rotational symmetry is rather unexpected and was evidence of a nematic state at the interface. The next section is devoted the measurements we conducted to identify the energy scale of this nematic state, and a comparison of the nematic state we observe at the (111) LAO/STO interface to nematic states observed in other systems.

4.1.3. Evidence of an Electronic Nematic State

In the last few sections, I have described our surprising observation of anisotropy that exists in nearly every electronic property of the (111) LAO/STO interface,^{31,32} and our work which used post-growth treatments to show that the anisotropy "lives" in the STO Ti bands intrinsic to the interface.³² In this section, I will present work which identifies the temperature range at which this anisotropy onsets, compare its amplitude to other material systems, and present a model to explain our results.³³

Before I dive into the temperature dependence of the electronic properties, I would like to note that the all of data sets presented in this subsection were taken on a different sample from the data sets in the first two subsections. The sample chip discussed in this section is Sample A7, and I have dubbed it the "nematic" sample for reasons that will soon become apparent. The nematic sample was an as-grown sample that was similar to the previous devices in that it displayed good atomic terraces that were oriented at 45° to the Hall bar devices, and the electronic properties were qualitatively similar to those seen in the previous samples chips.³³ The difference between the nematic sample and the other as-grown samples is the anisotropy onsets strongly at a more positive V_g ³³, yielding an $r_{aniso} \approx 5$ at $V_g = 45$ V, and the [110] direction became more resistive at a higher positive V_g .³³ Figure 4.11(a) shows that R_L along the [110] direction rose 10 k Ω/\Box with < 5 V change in V_q , far quicker than the O₂ annealed samples,^{32,33} which increased by the same amount over 40 V.³² In fact, by $V_g = 35$ V, $R_L > 300$ k Ω/\Box . From the previous sections, this sharp rise in anisotropy and R_L indicated that the nematic sample had fewer oxygen vacancies and lower disorder than the previously measured samples. Thus the results of our measurements primarily stemmed from the bands intrinsic to the interface. $^{30-32}$

The nematic sample was measured on a home built 1K cryostat whose heater had been replaced with a higher power resistive heater (a 1/2W 1 k Ω resistor) so that a wider range of temperatures could be accessed. These temperatures were monitored by a Lakeshore DT-670 calibrated silicon diode thermometer³ and a homemade temperature bridge.¹²¹ Each R_L vs T trace takes 16 hours for a full up and down sweep to ensure the trace and retrace of the two sweeps. Figure 4.11(b) shows the R_L vs T traces for both in-plane

³http://www.lakeshore.com/products/Cryogenic-Temperature-Sensors/Silicon-Diodes/DT-670/Pages/Overview.aspx



Figure 4.10. Averaged R_L vs V_g and Temperature dependence of R_L : (a) Averaged R_L vs V_g for both in-plane crystal direction on the "nematic" sample A7. The data was taken at T = 4.4 K (b) R_L vs T at $V_g = 50$ V. Figure and captions adapted from Davis *et al.*, Ref. 33.

directions measured simultaneously at $V_g = 50$ V, with an I_{ac} of 20 nA to avoid any spurious heating effects.³³ As expected at high temperatures, $25 \leq T \leq 40$ K, R_L in the [110] direction was identical to the [112] direction,³³ while at low temperatures, T = 4.4K, R_L was anisotropic as expected from Figure 4.11(a). At intermediate temperatures R_L smoothly transitions from the isotropic high temperature behavior to the anisotropic low temperature behavior, starting at $T \sim 22$ K.³³ We repeated this measurement for



Figure 4.11. Temperature Onset of R_L Anisotropy: (a) R_L vs T for the $[\bar{1}\bar{1}2]/[1\bar{1}0]$ directions in red/black measured simultaneously on sample A7 at $V_g=50$ V. Measurable anisotropy can be seen below ~ 22 K. Figure and captions adapted from Davis *et al.*, Ref. 33.

a range of V_g , and found that while the magnitude of the anisotropy changes with with V_g , the temperature at which the anisotropy onsets at a fairly constant characteristic temperature of $T \sim 22$ K.³³ We have designated this temperature T_{nem} as the anisotropy in (111) LAO/STO interface seems to stem from a nematic phase, which breaks rotational symmetry but maintains translational symmetry in the plane of the sample.³³ Curiously, for temperatures $T < T_{nem}$, R_L showed an activated temperature dependence. Figure 4.12(a) shows R_L plotted on a logarithmic scale as a function of T^{-1} for $V_g = 50$ & 55 V. The activated behavior was clearly seen in the near perfectly linear dependence on T^{-1} for $T^{-1} \leq .05$ K⁻¹. We fit this linear behavior to the Arrhenius function $R_{\Box} \sim e^{T_A/T}$.³³

quite well below T_{nem} and allowed us to extract the resulting activation temperatures T_A . Figure 4.12(b) shows T_A for both in-plane crystal directions. For $V_g \ge 70$ V the activation energies were isotropic, while below $V_g < 70V T_A$ s for the [110] and [112] directions were different and the [110] direction exhibited the higher of the two energies.



Figure 4.12. Anisotropy Activated Transport and Activation Energies: (a) R_{\Box} vs 1/T for $V_g=50$ V and 55V superimposed with fits to activated behavior as described in the text. (b) Plots of the extracted activation temperatures T_a vs V_g for the $[\bar{1}\bar{1}2]/[1\bar{1}0]$ directions in red/black respectively. All data is from sample A7. Figure and captions adapted from Davis *et al.*, Ref. 33.

As I have previously discussed, similar in-plane anisotropy has been observed in materials such as $Sr_3Ru_3O_7$,⁹⁴ iron-pnictide superconductors $Ba(Fe_{1-x}Co_x)_2As_2$,^{34–36} and other two dimensional electron gasses, such as $GaAs/Al_xGa_{1-x}As$ heterojunctions.³⁷ In the GaAs/Al_xGa_{1-x}As heterojunctions, this in-plane anisotropy stems from a striped charge density wave state that arises in the $\nu = 9/2$ quantum Hall state, and manifests an r_{ansio} of up to 15.³⁷ On the other hand, in the iron-pnictides, the in-plane anisotropy is driven by a complex interplay of a tetragonal to orthorhombic structural transition,³⁴ the onset of charge³⁶ and spin order,³⁵ which promotes a robust nematic phase that is tuned by temperature, doping, and magnetic field. This nematic behavior shows a smaller $r_{aniso} \approx 2$, but like the LAO/STO interface, plays host to a multitude of complex phases such as superconductivity and magnetism.^{34–36}

In the iron-pnictide and cuprate superconductors, another measure of anisotropy arising from a nematic state is the degeneracy in the carrier densites, ³⁶ n, of the Fe d_{xz} and d_{yz} measured by ARPES lifts.³⁶ In LAO/STO, the 2DCG is buried beneath the insulating LAO; thus, we cannot directly utilize ARPES to examine the 2DCG in (111) LAO/STO samples. We could, however, measure R_H as a function of temperature and V_g .³³ As I discussed previously, while we could not extract exact carrier densities from R_H , we know that R_H should be isotropic for materials like LAO and STO, which have cubic or tetragonal symmetry.^{31,32,99,100,102} Thus, any anisotropy in R_H would be further evidence of nematic order at the interface.³⁶ Figure 4.13(a) shows R_H measured simultaneously as a function of T for $V_g = 50$ V. R_H in the [$\bar{1}\bar{1}2$] and [$1\bar{1}0$] directions is isotropic above T_{nem} ;³³ on the other hand, below T_{nem} , $|R_H|$ along the [$1\bar{1}0$] decreases more rapidly than along the [$\bar{1}\bar{1}2$] direction. Figure 4.13(b) shows the results of similar measurements conducted over the same range of V_g as in Figure 4.12. For clarity I have plotted the ratio of Hall coefficients, $r_H^{aniso} = R_{H_{[110]}}/R_{H_{[112]}}$.³³ This plot confirms that similar to R_L , the anisotropy in R_H only occurs for $V_g < 70$ V and only below T_{nem} . This implied that the transitions to anisotropic behavior R_L and R_H were manifestations of the same nematic state.³³



Figure 4.13. Temperature Onset of R_H Anisotropy For Sample A7: (a) The Hall coefficient R_H vs. temperature T for the $[\bar{1}\bar{1}2]$ and $[1\bar{1}0]$ directions in red and black respectively, measured simultaneously at V_g =50 V. (b) The ratio $r_H^{aniso} = R_{H_{[1\bar{1}0]}}/R_{H_{[\bar{1}\bar{1}2]}}$ of the Hall coefficients along the two crystal directions vs. T for different V_g . (c) Schematic representation of a system with anisotropic band edges. The solid parabolic bands represent the $[\bar{1}\bar{1}2]/[1\bar{1}0]$ directions in red and black respectively, the horizontal lines represent the Fermi energy at different values of V_g , and the orange dashed lines represent defect states at the interface. Figure and captions adapted from Davis *et al.*, Ref. 33.

With these observations in mind we have built a model to explain the mechanism by which the anisotropies in R_H and R_L manifest.³³ As shown schematically in Figure 4.13 the model involves a splitting of the band minima in the $[\bar{1}\bar{1}2]$ and $[1\bar{1}0]$ directions, where the band in the $[\overline{1}\overline{1}2]$ direction has a lower band edge than in the [110] direction. If we consider the case when scattering between bands is suppressed, then when V_g has a high positive value the Fermi level is positioned such that bands along both directions are fully occupied and no anisotropy is observed.³³ In the nematic Sample A7 this corresponds to $V_g = 70$ V. As V_g is lowered, the Fermi level first drops below the band edge for the $[1\overline{1}0]$ direction and the [112] direction second. When the Fermi level is below the band edge in a particular direction, the only method of conduction through the band is by thermal excitation of localized levels in the gap,³³ likely oxygen vacancy defect levels.^{33,133,142} At intermediate V_g , ≈ 60 V for the nematic samples,³³ the Fermi level is below the $[1\overline{1}0]$ direction, but the [112] direction is still populated. This leads to the small anisotropy that is observed with very small T_A . At low V_g , ≈ 50 V for the nematic samples, the Fermi level is below both band edges, but far below the edge in the $[1\overline{1}0]$ direction leading to a large anisotropy and larger activation energy into the $[1\overline{1}0]$ band.³³

The key ingredient to preserving this nematic state is the suppression of scattering between the bands, otherwise any anisotropy would be washed out by the disordered nature of the interface.^{31–33} One mechanism that could provide the suppression of scattering, even in the presence of disorder, is strong spin-orbit coupling.^{28,107} In systems with strong spin-orbit coupling, the spins can become locked to momentum of the charge carriers,^{28,107} and thus, a carrier can only scatter to another band if its spin is also flipped in the scattering event. It is well documented that strong-spin orbit interactions exist at the LAO/STO interface^{12, 16, 19, 62} and lead to the splitting of otherwise degenerate band edges.^{12, 62} Furthermore, it has been theoretically predicted that at the (111) LAO/STO interface, the large spin-orbit will explicitly stabilize nematic behavior in the form of a charge density waves or spin density waves depending on the strength of the spin-orbit interaction.^{12, 151} Structural transitions could also give rise to the anisotropy we see,^{34, 94, 150} especially if there is an ordered orthorhombic symmetry at the interface. However, the only reports of ordered orthorhombic STO sturctures occured in STO with more than 33% O-18 substituted into the oxygen sites,⁷⁴ or in STO that has had extremely large stresses placed on the crystal.¹⁵² Furthermore, this tetragonal to orthorhombic transition occurs at $T \approx 60$ K, far away from $T_{nem} \sim 22$ K.^{74, 152}

While direct observation of a nematic state would require a local probe, such as low temperature scanning capacitance microscopy, what I have shown in this section is strong evidence that an electronic nematic state exists at the interface. This is, to my, knowledge the first observation of such a state at the LAO/STO interface, and may display states which combine already observed effects, such as superconductivity, with the broken symmetries involved with the nematic state in a gate tunable system. In the next sections I will discuss the superconducting state at the interface and the evidence that the anisotropic nematic state persists into the superconducting state.

4.2. Measurements for $T \leq 4 \ K$

While the previous sections covered our observations of the surprising anisotropy at the (111) LAO/STO interface, they focused on data that was taken at $T \gtrsim 4.4$ K.^{31–33}

However, many of the most fascinating phenomena occur at extremely low temperatures. For instance, superconductivity has been observed to only exist at $T \leq 300 \text{ mK}$;^{5–7} additionally, the coexistence of this superconductivity with ferromagnetism has also only been observed at these ultra low, mK temperatures.^{20,23,125} In this chapter I will describe the superconductivity and ferromagnetism that we observe at the interface, as well as the sometimes strong anisotropy that coexists with these low temperature effects.

4.2.1. Superconductivity at the (111) LaAlO₃/SrTiO₃ Interface

Superconductivity at the LAO/STO interface has been well documented.^{5-7, 20, 23, 125} In fact, it is this superconductivity that drove much of the early research into the material. As I briefly discussed in Chapter 2, superconductivity at the LAO/STO interface was fascinating to researchers as its properties, most notably its superconducting transition temperature T_C , could be tuned *in-situ* via a backgate voltage, V_g . Both T_C and the superconducting critical current I_C showed a dome like dependence similar to be the cuprate superconductors,^{5,7,20,23,125,153,154} and the superconductor carrier gas was shown to accurately described as a 2D system.^{7,20,23,125} Further investigation as to the nature of this superconductivity have been conducted by a variety of groups, who have confirmed the BCS-like nature of the superconducting state.^{155,156} Beyond the work discussed in Chapter 2, Richter *et al.*¹⁵⁵ have used tunneling spectroscopy in conjunction with simultaneous electrical transport to further characterize the superconducting behavior at the LAO/STO interface. They found that the superconducting gap is well described by a single BCS gap function, and can be treated like a more conventional thin film superconductor.^{155,156} A characteristic we have used to determine the thickness and coherence length of the superconducting 2DCG in our (111) LAO/STO heterostructures.²⁹ More interestingly, they found that although T_C showed a dome like behavior, where T_C reduced to 0 when V_g was decreased to large negative values (and thus lower n);¹⁵⁵ the superconducting gap Δ continued to grow even as T_C was reduced.¹⁵⁵ The gap persisted even as the 2DCG became normal, indicating that preformed Cooper pairs play an important role in the material even when they lack global phase coherence,¹⁵⁵ similar to the cuprate materials, TiN,¹⁵⁷ and other 2D Fermi gasses.¹⁵⁸ In contradistinction to these results, tunneling measurements on Nb doped SrTiO₃ showed that while T_C continued to show a dome like dependence on n,^{42,43,46,163,164} Δ followed the T_C . Richter *et al.*¹⁵⁵ as well as other theoretical and experimental groups postulated that this difference is due to the 2-D nature of the LAO/STO interface and may indeed be universal to all 2D superconductors.¹⁵⁵ In the following discussion of the superconducting properties of the (111) LAO/STO interface, I will highlight not only the deviations from the behavior seen in (001) LAO/STO heterostructures, but also the deviations from what one would expect from bulk superconductors.

Returning to our measurements, after the samples were characterized at $T \approx 4.4$ K, they were cooled to mK temperatures using either a Oxford Kelvinox 300 or Kelvinox MX100⁴ dilution refrigerator. In these measurements the excitation current was maintained at $I_{ac} \approx 10$ nA to ensure that any thermal broadening was minimized.²⁹ Figure 4.14 shows the temperature dependence of R_L for samples A1, H4, and O3, (a)-(c) respectively. Figure 4.14(a) shows that the as-grown sample A1 exhibited no superconducting

 $^{{}^{4}} https://www.oxford-instruments.com/products/cryogenic-environments/dilution-refrigerator/wet-dilution-refrigerators/dilution-refrigerator-kelvinox400 ha$


Figure 4.14. R_L vs T for the (111) LAO/STO Heterostructures: R_L vs T for the (a) as-grown A1, (b) Ar/H₂ annealed H4, and (c) O₂ annealed O3 samples. (a) is taken at $V_g = 0$ V. Figure and captions adapted from Davis *et al.*, Ref. 31, Ref. 30, and Ref. 29.

transition at $V_g = 0$. Indeed the sample did not show any sign of a superconducting transition in the temperature dependence at any V_g , indicating that at least at first glance, that there was no superconductivity in the (111) LAO/STO samples.^{29,31} Figure 4.14(a) also shows that the anisotropy continued to increase in amplitude with decreasing temperature, and the two directions showed different dependencies: the [110] direction showed insulating behavior, and the [112] direction showed a near constant R_L as a function of $T.^{31}$

Figure 4.14(b) shows that when oxygen vacancies were added by Ar/H_2 annealing, sample H4 began to exhibit superconducting transitions with T_{C} s of ≈ 235 mK and ≈ 283 mK for samples cooled at $V_g = 50$ and -10 V respectively.²⁹ The increase of T_C with decreasing V_g and n showed that (111) LAO/STO interfaces also exhibit dome like behavior in T_C , like both the (001) LAO/STO heterostructures and the Nb doped $STO.^{7,20,23,29,42,43,46,125,163,164}$ It was tempting to attribute the existence of superconductivity at the interface to either the increase in carrier density due to oxygen vacancies, or the oxygen vacancy defect states themselves.²⁹ However, if this were true, the O_2 annealed sample O3 would have shown no signs of superconductivity as it had fewer vacancies than the as-grown sample A1 which was not superconducting at any temperature or V_g . Suprisingly the oxygen annealed sample O3 also showed signatures of superconductivity at positive V_g .²⁹ Figure 4.14(c) shows that when the O₂ annealed sample O3 was cooled from 4 K to 30 mK at $V_g = 50V$, it showed an incomplete superconducting transition at $T \approx 80$ mK in both directions.²⁹ The resistance continued to decrease as temperature was lowered; however, even at the lowest measurable temperatures, 15 mK, both directions still exhibited a non-zero resistance.²⁹



Figure 4.15. Differential Resistance Vs I_{dc} for the Ar/H₂ Annealed Samples: dV/dI vs I_{dc} at a range of V_g for the Ar/H₂ annealed sample H4 (a)/(b), and the O₂ annealed sample O3 (c)/(d). Both samples were measured at $T \approx 30$ mK after the samples were cooled at $V_g = -10$ V. Figure (a)/(b) and captions are adapted from Davis *et al.*, Ref. 30

To further investigate the nature of the superconductivity, or near superconductivity, at the interface, we measured the differential resistance, dV/dI, as a function of dc current, I_{dc} , applied along the length of the sample after the samples were cooled from $T \approx 4.4$ K to 30 mK at a $V_g = -10.^{29}$ Figure 4.15(a)/(b) and (c)/(d) show the results of these measurements over a range V_g for the Ar/H₂ and O₂ annealed samples respectively. In the Ar/H₂ annealed sample H4, both directions exhibit a zero resistance state at positive V_g .²⁹ This zero resistance state disappears for negative values of V_g , at $V_g < -50$ V for the [110] direction and $V_g < -70$ V for the [112] direction. However, even at the most negative values of V_g , both crystal directions displayed a substantial drop in R_L near $I_{dc} = 0$ nA. This drop in R_L indicated that superconducting correlations persisted even for the lowest V_g ; similar to the pseudo gap behavior discussed earlier on the (001) LAO/STO heterostructures,^{155,156} TiN thin films,¹⁵⁷ and cuprate superconductors.^{153,154} Even though the O_2 annealed sample O3 did not exhibit a zero resistance state, Figure 4.15(c)/(d) shows that the dV/dI vs I_{dc} response still showed the same pseudo-superconducting behavior seen at lowest negative V_g in the Ar/H₂ sample H4.²⁹ Again, this behavior implied that superconducting correlations existed in the O_2 annealed sample $O3.^{29,155,157}$ Unlike the Ar/H_2 annealed sample H4, the O_2 annealed sample O3 showed a transition to a nominally insulating state.²⁹ However, this state had a very odd dependence on I_{dc} . R_L rapidly decreased with increasing $|I_{dc}|$ forming a peak, which was symmetric about $I_{dc} = 0$. This peak had a width similar to the gap and may be be evidence of a state similar to the Cooper pair insulator state seen in TiN and Al thin films.¹⁶⁰

More striking was the observation that the superconducting(psuedo) state of both the Ar/H₂ and O₂ annealed samples (H4 and O3) exhibited large anisotropy in amplitudes and characteristics of I_C . Defining I_C as the maximum in dI/dV over the full range of I_{dc} , the results of these analyses are shown in Figure 4.16 (a) & (b), where (a) corresponds to the Ar/H₂ annealed sample H4 and (b) to the O₂ annealed sample O3.²⁹ The Ar/H₂ devices on sample H4 showed little to no anisotropy at the most negative V_g , as expected based on results at $T \approx 4.4$ K. As V_g was increased to more positive values, I_C grew in



Figure 4.16. Critical Current vs Backgate Voltage for the O₂ annealed and Ar/H₂ annealed samples: I_C vs V_g for the (a) Ar/H₂ annealed sample H4 and (b) the O₂ annealed sample O3. Sample cooled from 4.4K at $V_g = -10$ V. Figure (a) is adapted from Davis *et al.*, Ref. 30.

both directions, but much faster in the $[\bar{1}\bar{1}2]$ direction compared to the $[1\bar{1}0]$ direction.²⁹ The O₂ annealed sample O3, on the other hand, showed a strong dome like behavior along both crystal directions, where " I_C " was larger in the $[1\bar{1}0]$ direction. More specifically the width of the dip in R_L near $I_{dc} = 0$ nA was larger in the $[1\bar{1}0]$ direction than in the $[\bar{1}\bar{1}2]$ direction over the entire V_g range.²⁹ This anisotropy in the superconducting state was rather unexpected and points the possibility of an unconventional superconducting state. Indeed, many of the properties of the LAO/STO superconducting state were reminiscent of the cuprate superconductors, which experiments have found to have *d*-wave superconductivity.^{153,154,159} Tunneling measurements conducted on the (001) LAO/STO interface did not rule out the possibility of these lower symmetry order parameters,¹⁵⁵ and in fact there have been theoretical studies that predict *d*-wave superconductivity in (001) LAO/STO.¹² Another possible explanation for this anisotropy could be that the superconductivity in this system is multiband in nature, where there are multiple s-wave gaps. Theoretical studies have shown that a multigap s-wave superconductor coupled with a charge density wave state could lead to anisotropy in the superconducting properties.¹⁵⁹ This scenario is aided by the fact that there as been direct observation of two band superconductivity in a variety of STO systems,^{43,165} including Nb:STO and (001) LAO/STO.^{156,166} Detracting from this theory is the fact it would yield an anisotropic superconducting T_C vs $\mu_0 H$ dependence, which is not observed in either system.¹⁵⁹

Either scenario would require spectroscopic measurements of the system to confirm its accuracy; unfortunately, we have not conducted tunneling measurements to directly investigate the order parameter at the interface. We have, however, conducted careful magnetoresistance measurements, which gave greater insights to both nature of the superconducting state and the physical dimensions of the 2DCG. The results of these magnetoresistance measurements are the subject of next section.

4.2.2. Magnetoresistance in the Superconducting State: Coexistence

The response of the LAO/STO system to magnetic fields has proven to be an invaluable tool, not only for identifying the carrier type and density as we did in previous sections,³¹⁻³³ but also for identifying the superconducting critical fields,^{6,7,20,23,125} the thickness of the superconducting 2DCG,^{20,23,125} identifying the existence of a quantum critical transition,^{23,161} and most importantly, observing the coexistence of superconductivity and magnetism at the interface.^{20,23,125} The coexistence of superconductivity and ferromagnetism rarely occurs in materials as the spin singlet Cooper pairs in s-wave superconductors are broken by the exchange field of the ferromagnet.¹⁴⁹ In LAO/STO, magnetoresistance (MR) measurements have shown that the ferromagnetism interacts with the superconductivity primarily through the ferromagnet's external magnetic field.^{20,125} The data I will show in this section will exclusively deal with the Ar/H₂ annealed sample H4. Unfortunately, the O₂ annealed sample O3 exhibited so much drift, as described in Chapter 3, that measuring MR was not feasible. Figure 4.17 shows R_L as a function perpendicular magnetic field for the Ar/H₂ annealed sample H4 measured simultaneously along both in-plane directions at 30 mK at $V_g = -30$ V after being cooled through the superconducting transition at $V_g = -10$ V.

The most striking feature of the MR is shown in the inset where both the $[1\bar{1}0]$ direction and $[\bar{1}\bar{1}2]$ direction featured hysteretic peaks centered at $\mu_0 H \perp = 32 \text{ mT}.^{29}$ These peaks were direct evidence of the coexistence of superconductivity and ferromagnetism at the (111) LAO/STO interface.^{20,23} Similar to the evidence of coexistence seen in the (001) LAO/STO heterostructures, these hysteretic peaks were rate dependent,^{20,23} where increasing the rate yielded larger peaks. Thus all of the MR data in this thesis was taken at a constant sweep rate of 0.21 mT/s unless otherwise noted. As a reminder, the peaks are associated with the magnetization dynamics of the ferromagnetic domains at the interface.^{20,23} Additionally, similar to the as-grown samples, at $T \approx 4.4$ K the longitudinal MR is perfectly flat within our measurement resolution ($\approx 5 \Omega$) so the ferromagnetism, or our sensitivity to it, is restricted to mK temperatures.²⁹ In this case we have found that the ferromagnetism dies out in these structures near $T \approx 400$ mK.



Figure 4.17. Hysteretic Magnetoresistance in the Superconducting State: Magnetoresistance (MR) of the $[\bar{1}\bar{1}2]$ and $[1\bar{1}0]$ Hall bars at 30 mK, at a back gate voltage of V_g =-30 V. Inset: Expanded plot of the MR near zero field, showing the hysteresis in magnetic field. All data comes from sample H4. The sample was cooled from 4.4 K to 30 mK at $V_g = -10$ V Figure and captions adapted from Davis *et al.*, Ref. 30.

The gate dependence of the MR is shown in Figures 4.18(a) & (b) for the [110] and $[\bar{1}\bar{1}2]$ directions respectively.²⁹ Due to the wide range of R_L accessed with decreasing V_g , I normalized the data to the normal state resistance (R_N) , defined as the value of dV/dI at T = 30 mK and $I_{dc} = 2.5 \ \mu \text{A.}^{29}$ Additionally, Figure 4.17 shows that the sweeps are mirror symmetric around $\mu_0 H_{\perp} = 0$ mT; thus, for clarity, I have only shown the sweeps from ~ -600 mT to ~ 600 mT. When normalized in this manner it is clear that the change in R_L as a function of $\mu_0 H_{\perp}$ is a significant fraction of R_N , qualitatively similar to the response seen in the (001) LAO/STO heterostructures, but quantitatively larger.^{20,23} In fact at $V_g = -90$ V, this background MR response exceeds the normal state resistance



Figure 4.18. Hysteretic Magnetoresistance vs V_g : (a), (b) Normalized MR for the [110] (b) and [112] (c) crystal directions, at 30 mK, for various gate voltages. For clarity, only the sweeps from negative to positive magnetic field are shown. All data taken on sample H4. The sample was cooled to 30 mK at $V_g = -10$ V. Figure and captions adapted from Davis *et al.*, Ref. 30.

(by a significant amount in the case of the $[\bar{1}\bar{1}2]$ direction) and does not saturate for any V_g and is hysteretic over the entire field range. The lack of saturation in the longitudinal

MR is a sharp departure from the behavior in (001) LAO/STO devices, which exhibited a rapidly saturating MR at relatively low fields ($\approx 150mK$), which also showed little hysteresis after the MR had saturated.^{20,23} Experiments in (111) LSAT/STO indicate that this hysteresis might be due to large spin orbit coupling at the interface, however it could also be tied to the more glassy nature of the interface. The dependance of the background MR also showed a host of interesting features. For instance, at positive V_q the shape of the background MR is quadratic in $\mu_0 H_{\perp}$ with a positive second derivative for $\mu_0 H_{\perp} \geq 50 \text{ mT.}^{29}$ As V_g was lowered to $V_g = -90V$, this positive quadratic curvature changed into a linear dependece in the case of the [110] direction and slight negative curvature in the [112] direction. Again in both directions this curvature, or lack there of, persisted into what is nominally the normal state of the system as a function of field. The linear MR in the [110] direction was especially striking as it was nearly perfectly linear from $\pm 600 \rightarrow 0$ mT, and slightly exceeded the normal state resistance.²⁹ Similar linear behavior has been reported in topological insulators where it was associated with Dirac bands in the lowest lowest Landau level.¹¹⁶ Further experiments utilizing higher magnetic fields applied both perpendicular to and in the plane of the sample to could be performed to elucidate the origins of this linear MR. Unfortunately these higher field measurements were outside the scope of this thesis but could be conducted by future students.

Finally we have utilized the feedback method described in Chapter 3 to continuously measure the T_C vs $\mu_0 H$ phase diagram with the magnetic field applied both perpendicular and parallel to the plane of the sample. For the [110] direction in the Ar/H₂ annealed samples at $V_g = 100$ V, we set the balance resistor $R_{bal} = R_L = 4.2$ k Ω which corresponded to the midpoint of the resistive superconducting transition. We have defined the temperature



Figure 4.19. T_c vs $\mu_0 H$ Phase Diagrams: (a) Superconducting transition temperature T_c as a function of perpendicular magnetic field for the $[1\bar{1}0]$ Hall bar for $V_g=100$ V. The line with symbols is a fit to the linear dependence.(b) T_c as function of parallel magnetic field for the $[1\bar{1}0]$ Hall bar for $V_g=100$ V. The line with symbols is a fit to a quadratic dependence. (c) T_c as a function of perpendicular magnetic field for the Hall bar devices $[1\bar{1}0]$ and $[\bar{1}\bar{1}2]$ for $V_g=100$ V. (d) T_c as a function of perpendicular magnetic field for the $[1\bar{1}0]$ Hall bar for $V_g=100$ and -50. All data take on sample H4. The sample was cooled from 4.4 K at $V_g = -10$ V. Figure (a) & (b) and the respective captions adapted from Davis *et al.*, Ref. 29

at which this value of R_L occurs to be T_C .²⁹ The resulting T_C vs $\mu_0 H_{\perp,||}$ phase diagrams for the [110] direction are shown in Figure 4.19(a) & (b) for $\mu_0 H_{\perp}$ and $\mu_0 H_{||}$ respectively. By analyzing this phase diagram we were able to extract the Ginzburg-Landau superconducting coherence length, ξ_{GL} , as well as the thickness of the superconducting gas, d. The equations for this analysis can be found in Appendix C and derivations of the equations used to fit these phase diagrams can be found in a number of texts on superconductivity, or in a more complete form in the theses of Chandrasekhar or Santhanam.^{167,168}

In Figure 4.19(a) the phase diagram for perpendicular field shows the correct linear dependence and a small amount of hysteresis that was indicative of the ferromagentic order in the sample.^{20,125,167–169} After extracting the slope of this line to be $\approx 1.7 \text{ T/K}$, we found ξ_0 to be approximately 26 nm, in good agreement with results on the LAO/STO devices.^{7,20,23,40,125} Moving to Figure 4.19(b) we found that the phase diagram for T_C vs $\mu_0 H_{||}$ was more complex. The magnetoresistance exhibited not only the expected quadratic dependence on field, but also a hysteretic dip that was more significant compared to the overall size of the signal change. Again this hysteresis was a signature of the ferromagnetism living alongside the superconductivity and is discussed in greater detail elsewhere. To avoid the complication of the hysteretic peak we fit only the data for $|\mu_0 H_{||}| > 200$ mT. This function gave a $H_{c||} \approx 2.5$ T which yielded a thickness $d \approx 7$ nm. The value of d found here was taken at $V_g = 100$ V where the gas is expected to be at its maximum thickness. While the value of the ξ_0 is similar to values reported in the (001) LAO/STO heterostructure, d was nearly half the value of the (001) 2DEG thickness. We have conducted similar perpendicular field measurements for the both the [112] direction as well as at other values of V_g . As Figure 4.19(c) shows, we found that as V_g was decreased the coherence length shrank to $\xi_0 \approx 17$ nm at $V_g = -50$ V, the lowest voltage at which the both directions exhibit a zero resistance state. The reduction in the coherence length agrees with the increase in critical field with decreasing V_g that is seen in Figure 4.18, and indicated that the superconducting gap is actually getting stronger as V_g is lowered. This is in good agreement with tunneling measurements conducted on (001) LAO/STO,^{155,156} as well as results in TiN¹⁵⁷ and the cuprate superconductors.^{153,154,159}

On the other hand, Figure 4.19(c) plainly shows that the there was no discernible anisotropy between the directions in terms of ξ_0 . The fact that we observed no anisotropy in T_C or ξ_0 hints that the superconductivity at the (111) LAO/STO interface may not be anisotropic on its own, but instead combines normal *s*-wave superconductivity with a more complex, anisotropic, and possibly nematic state. These sorts of combined states have been predicted to play host to a variety of exotic phases and particles, such as Majorana fermions,^{28,156,159} and would benefit from investigations using local low temperature probes, such as ultralow temperature MFM, or more complex mesoscopic (111) LAO/STO structures, which could explicitly probe the nature of the gap and/or quasi-particles in the system. However, the aforementioned investigations are very involved projects that could each form the basis of a thesis on their own. In the last section of this thesis I would like to highlight an effect that we discovered that seems to be unique to the (111) LAO/STO interface.

4.2.3. Low Temperature Memory Effects

Disorder is known to affect the properties of superconductors, despite the fact that in s-wave superconductors, Anderson's theorem says they should be insensitive to such perturbations.^{162,170} Many conventional superconductors, such as niobium, show a decreased T_C with increased disorder;¹⁷¹ an effect explained via enhanced Coulomb interactions due to the shorter elastic mean free path. This led to a more inhomogeneous superconducting state, which in the limit of large disorder can transition to an insulating state, the

transition between the two is of course called a superconductor to insulator transition (SIT).^{171,176–178} In a few s-wave superconductors, such as a luminum, increasing disorder actually increases T_C , in some cases by up to a factor of 5.^{173,174} This change has been ascribed to a modification of the electro-phonon interaction responsible for the creation of phase coherent Cooper-pairs in the material.^{171,179,180} Another example of disorder affecting superconductivity comes from Nb doped $SrTiO_3$, which, while s-wave,^{163,166} shows a complex domed dependence on disorder induced through doping. This dome is ascribed to a mismatch that develops between the carrier densities in the superconducting and normal states as the Nb doped $SrTiO_3$ samples transition between the clean and dirty limits.^{163,166} Finally, superconductors with more exotic gap symmetries, like the d-wave cuprates or the f-wave heavy Fermion superconductors are exceptionally sensitive to disorder,^{153,154,159,181,182} whereby small amounts of disorder will completely kill off the superconductivity. However, in the aforementioned systems, the amount of disorder is locked into the sample at the time of growth, while in LAO/STO disorder can be tuned with V_q , giving rise to the gate-tunable SIT seen in our data as well as by many other groups.7,20,29,125

In addition to this gate tunability, we have found that the (111) orientation of the LAO/STO heterostructure hosts a surprising memory effect;³⁰ where the electronic properties of the (111) LAO/STO devices strongly depend on the gate voltage that the sample was cooled from ≈ 4.4 K down to mK temperatures. Even if V_g is subsequently changed at low temperatures the the overall electronic properties stay "frozen" into the sample until the sample is heated to $T \approx 4.4$ K.³⁰ I have dubbed the voltage at which the samples are cooled the freezing voltage, V_F .



Figure 4.20. Normalized Differential Resistance vs V_g vs I_{dc} for the Ar/H₂ Sample H4 The critical current I_c varies with V_g , a consequence of electrostatic doping by the gate, but is also a function of the freezing voltage V_F applied while cooling through the superconducting transition: in general, I_c is larger for $V_F = 50$ V in comparison to $V_F = -10$ V. For the Ar/H₂ annealed samples H4, there is relatively little anisotropy between the two crystal directions. Due to the large variation in R_N with V_g , the curves here and in Fig. 3 are normalized to the value of dV/dI at $\pm 1 \ \mu$ A. Figure and captions adapted from 29

The R_L vs T traces shown in Figures 4.14(b) & (c), for the Ar/H₂ and O₂ annealed samples (H4 and O3) respectively, are representative of the two freezing voltages that I will discuss in this section, $V_F = 50$ V and $V_F = -10$ V. For all of the data taken, V_g was repeatedly cycled from ± 100 V at $T \approx 4.4$ K in order to insure that any residual memory effects are reset.³⁰ After the cycling procedure, V_F was set by sweeping from $\pm 100V$ to the chosen V_F , and the sample was then cooled to T = 30 mK. The differences in the electronic behavior are most easily seen by reexamining the differential resistance dV/dI vs I_{dc} at different V_g for the two V_F .³⁰ In both the Ar/H₂ annealed samples and the O₂ annealed samples, the normal state resistance R_N changes by multiple orders of magnitude over the range of V_g ; thus, all of the data that I will present in this section was normalized to the R_N using the same method as in the last section. The results of the measurements for the Ar/H₂ sample H4 are shown as 3-D plots in Figure 4.20; where the x, y, and z-axis correspond to I_{dc}, V_g , and $\frac{1}{R_N} \frac{dV}{dI}$, respectively.³⁰ The top row shows the results for $V_F = -10$ V and is similar to the results shown in Figure 4.15(a) & (b), where the critical current changes with V_g and the zero resistance state disappeared for both crystal directions for negative V_g .³⁰ However, when the sample was cooled at $V_F = 50$ V the I_C increased drastically, almost doubling at most positive V_g , while the zero-resistance state at negative V_g disappeared entirely.³⁰ More subtle features like sub peaks in the critical current also appeared. All of the changes, both overt and subtle, were persistent with repeated sweeps of V_g , I_{dc} , and $\mu_0 H_{\perp}$.

Figure 4.21 shows similar data for the O_2 annealed sample O3. Recall these samples did not exhibit a zero resistance state at any V_g or any temperature.³⁰ Nevertheless, a dip in the differential resistance can be seen for both values of V_F ; and, as discussed before, the O_2 annealed sample O3 displayed a dome-like behavior in the pseudo I_C for $V_F = -10$ V.³⁰ When the sample was cooled at $V_F = 50$ V this freezing effect was even more apparent than in the Ar/H₂ samples, increasing not only I_C , but expanding the dome like behavior so that it extended beyond the most positive V_g measured.³⁰

I will now return to the Ar/H₂ annealed sample H4, which exhibits a zero resistance state and thus can be more cleanly analyzed. Figure 4.22 shows the I_C as a function of V_g and V_F where, due to the complex multi-peak structure in the $V_F = 50$ V, we



Figure 4.21. Normalized Differential Resistance vs V_g vs I_{dc} for the O₂ Sample O3: While the O₂ annealed sample O3 did not go fully superconducting, there is clear evidence for incipient superconductivity in the current-voltage characteristics, even for $V_F = -10$ V, for which the resistance increases with decreasing temperature (Figure 4.14(c)). As with the Ar/H₂ annealed sample H4 (Figure 4.20), the superconducting characteristics change with V_g , a consequence of electrostatic doping, but also are a function of the voltage V_F at which they are cooled. Figure and captions adapted from Ref. 29

have defined the I_C as the point where $d^3V/dI^3 = 0$, i.e. the point where the slope of R_L rise was maximum.³⁰ As expected, I_C was larger at more positive V_g and V_F , and overall the I_C curve seemed not to shift along the V_g axis, but increased I_C , almost uniformly. This trend made it apparent that changes in V_F not only changed the carrier concentration at the interface, but also more complex interactions, such as the dependence of the superconducting properties on V_g .³⁰ To further investigate these properties we examined the R_N and T_C continuously as a function of V_g , where R_N was defined as the



Figure 4.22. I_C , R_N , and T_C vs V_g for the Ar/H₂ annealed sample H4: Critical current I_c (a), normal state resistance (b) for the Ar/H₂ annealed samples for freezing voltages $V_F = -10$ V and $V_F = 50$ V, for both the [$\bar{1}\bar{1}2$] and [$1\bar{1}0$] crystal directions, taken from Fig. 2. Since the data show multiple peaks, I_c is defined to be the value of I_{dc} at which the slope of dV/dI vs I_{dc} is a maximum $(d^3V/dI^3 = 0)$. R_N was defined as the value of dV/dI at $I_{dc} \pm 1 \mu A$. (c) Critical temperature T_c as a function of V_g , measured using feedback techniques by biasing the device at the foot of the superconducting transition while sweeping V_g . Figure and captions adapted from Davis *et al.* Ref. 29.

value of dV/dI at $I_{dc} \pm 1 \ \mu$ A. Figure 4.22(b) shows that traces of R_N shifted with changes in V_F , becoming more resistive at more positive values of V_g , indicating that even in the normal state the (111) LAO/STO system was affected by disorder.³⁰ To continuously measure T_C as a function of V_g we used the same technique used to measure the T_C vs $\mu_0 H$ phase diagram, except in this case we swept V_g instead of field.³⁰ Figure 4.22(c) shows that for both values of V_F the two directions exhibited an isotropic T_C over the range of V_g . More importantly, it showed that the dependence of T_C on V_g is different depending on V_F and could not be scaled by moving the curves along either the V_g or T_C axis.

The observation that different V_F yielded different dependences of T_C on V_g coupled with the fact that T_C decreases while I_C increases implied that, similar to the the effects observed in Al films,^{173,174} we may be modifying the attractive electron-phonon interaction.^{171,179,180} An easier way to visualize such a modification is to return to the superconducting dome picture in the T_C vs n phase diagrams of the cuprate superconductors.^{153,154,159} In this picture our results show that we were not simply shifting along the axis of the diagram, but instead we were expanding or contracting the dome with different V_F .

A final indication of the strength of this freezing effect could be seen in the change in magnetoresistance (MR) as a function of V_g after cooling at different V_F . Figure 4.23(a) & (b) shows the normalized MR traces for $V_F = -10$ V and 50 V respectively. The most obvious change in the MR was that when the samples were cooled at $V_F = 50$ V there was no transition out of the superconducting state.^{29,30} The second observed change was that the dependence of the hysteretic peak amplitude on V_g was reversed between the two



Figure 4.23. Frozen in Magnetoresistance vs V_g for the Ar/H₂ Sample H4: Normalized magnetoresistance along the [110] direction for (a) $V_F = -10$ V and (b) $V_F = 50$ V. All data taken on the Ar/H₂ annealed sample H4. Figure and captions adapted from Ref. 29

values of V_F . For $V_F = -10$ V, the peak decreases in normalized amplitude as V_g was increased, on the other hand for $V_F = 50$ V the peak amplitude actually increased with V_g and was a much larger fraction of the overall resistance change.^{29,30} Finally, it was clear that the dependence of $H_{c\perp}$ on V_g was also strongly modified as a function of V_F , where for $V_F = -10$ V the $H_{c\perp}$ was non-monotonic with increasing V_g while for $V_F = 50$ V it monotonically increased with increasing V_g . Again this was a clear indication that we were changing the actual phase diagram of the superconductivity, not just shifting it around.

The preceding discussion established that at some temperature between $T \approx 4.4$ K and T = 30 mK changes to the sample's electronic properties are frozen in based on the V_g maintained at the time of cooling. These changes affect all of the system's electronic properties, and the frozen in electronic properties were stable on the time scale of weeks, and against changes in I_{dc} , V_g , and $\mu_0 H$ provided that the sample was not raised above a certain temperature, T_F .³⁰ We determined T_F by performing systematic R_L vs V_g sweeps using the following procedure: first V_g was cycled at 4.4 K to clear any residual memory effects; V_g was then swept to the target V_F from +100 V; the sample was then lowered to the desired testing temperature; once the target temperature was achieved, V_g was swept and R_L was measured along both directions simultaneously; and finally the temperature was raised back to 4.4 K and the procedure was repeated.³⁰ The results for the Ar/H₂ annealed samples along the [112] direction at 4 target temperatures of 30 mK, 470 mK, 675 mK, and 1.2 K are shown in Figure 4.24. At 1.2 K and 675 mK there was little to no difference between the two V_F . At 470 mK the differences between two V_F



Figure 4.24. Onset of the Memory Effects: Resistance of the Ar/H₂ annealed sample H4 in the [$\bar{1}\bar{1}2$] crystal orientation as a function of V_g after cooling from 4.4 K to the target temperatures noted with gate voltages $V_F = -10$ V and $V_F = 50$ V applied. As the resistance is hysteretic with V_g , the average of the upsweep and downsweep traces as a function of V_g is shown in each case. Differences between the curves for the two freezing temperatures show up only below 600-700 mK, showing that the freezing temperature T_F is of order ~ 0.6 K. Figure and captions adapted from Davis *et al.* Ref. 30.

almost 5 times smaller than the $V_F = -10$ V trace at negative V_g . Finally, at 30 mK the two traces showed nearly an order of magnitude of difference when the sample was not superconducting.³⁰ Thus we concluded the freezing effect onsets at $T_F \approx 575$ mK.

The extremely low energy that this memory effect onsets at rules out many of the previously discussed mechanisms which could serve as origins of this memory effect. For instance, a similar effect occurs in (001) LAO/STO heterostructures associated with an

irreversible change in the occupation of trapped charge states at the interface. In that case the relevent energy scale was room temperature (≈ 105 K).^{89,92} We observe a similar effect in the (111) LAO/STO samples: after first cooling the samples down from room temperature, there is an initial V_g trace that is irreproducible. However, the freezing effects I described above were stabilized at temperatures ≈ 175 times lower than the initial trapping effects. Thus if these effects are solely due to charge trapping a new physical mechanism would be required to explain the low energy scales. In my discussion of these effects I argued that these effects cannot solely stem from changes of carrier density at the interface; however, uncovering the exact origin and/or mechanism of the freezing effect requires further investigation. Again the perfect tool for such an investigation would be an ultra low scanning probe or tunneling microscope, both of which could locally probe the samples as a function of V_g , V_F , and T.

CHAPTER 5

Conclusions and Future Work

The 2DCG that forms at the interface between the band insulators LAO and STO has been studied due its rich phase space which contains many phenomena, including superconductivity and ferromagnetism. One of the main advantages of LAO/STO heterostructures over other transition metal oxide materials is the fact that the LAO/STO heterostructure's electronic properties are tunable with an *in-situ* electric field via an electrostatic backgate voltage. However, nearly all of the work done in the past decade has focused on the (001) orientation of the interface, which exhibits cubic symmetry at the interface.

In this thesis, I have described our extensive transport measurements characterizing the (111) orientation of the LAO/STO heterostructure. This orientation of the interface has hexagonal symmetry similar to graphene and the transition metal dichalcogenides; furthermore, due to this more complex symmetry, it has been predicted to show a number of exotic phenomena, including charge density waves, spin density waves, and topological insulating phases.

In order to determine if this more complex structural symmetry at the interface yielded more complex electronic properties, we fabricated Hall bar devices on the (111) LAO/STO sample chips , with two Hall bar devices along the [$\bar{1}\bar{1}2$] direction and two along the [$1\bar{1}0$] direction per sample chip. We measured the longitudinal resistance (R_L) and transverse resistance (R_{XY}) as functions of electrostatic backgate V_g , magnetic field $\mu_0 H$, dc current I_{dc} , and temperature and found a number of very interesting features. These features encompassed many of the phenomena seen in the (001) LAO/STO heterostructures, including superconductivity, ferromagnetism, and the coexistence of the two, traditionally antagonistic phenomena. Strikingly, we have observed that at temperatures below ≈ 22 K, the (111) LAO/STO interface showed robust anisotropy with respect to the in-plane crystal directions. This anisotropy appeared in nearly all of the of the samples' electronic transport properties and was surprising as the symmetry of the interface suggested that the conductivity matrix of the interface should be isotropic.^{99,100,102}

Nevertheless, we found that at 4 K, the longitudinal resistance R_L , Hall coefficient R_H , and temperature dependence of the system was anisotropic and could be strongly tuned with the application of V_g . In the response of R_L vs V_g , tuning to negative V_g caused the Hall bar devices in the [110] direction to drastically increase in resistance, becoming nearly 7 times greater than the resistance along the Hall bar device in the [112] direction. The anisotropy that we observed could not be attributed to terracing effects in the STO substrate or tetragonal domains at the interface, two sources of anisotropy documented in the (001) LAO/STO heterostructures. The Hall coefficient showed similar behavior, where at negative V_g , the R_H in the Hall bar devices along the [110] direction was smaller than in devices along the [112] direction. Additionally, the dependence of R_H on V_g showed that not only did multiple bands contribute to electronic transport in the 2DCG, but that one of these bands must be a hole band.

We also found that the anisotropy in the system was strongly dependent on the oxygen vacancy concentration at the interface and that the vacancy concentration could be changed via post-growth treatments such as annealing. Increasing the oxygen vacancy concentration in the LAO/STO samples by Ar/H_2 annealing completely suppressed the anisotropy in both R_L and R_H . In contrast, decreasing the oxygen vacancy concentration increased the amount of anisotropy present between the two in-plane directions. This tunability of the anisotropy with post growth treatment allowed us to localize the anisotropy to bands native to the interface rather than defect states in the system.

Measuring the dependence of both R_L and R_H as a function of temperature allowed us to identify that the anisotropy appeared at $T \approx 22K$. Below this temperature, R_L displayed strongly activated behavior with different activation energies along the two directions, implying that the band edges along the two directions were different. This behavior is strong evidence that an electronic nematic state exists at the interface; furthermore, such a nematic state has been predicted to exist at the (111) interface.¹⁰⁷ Further confirmation of this nematic state as well as an investigation of its spatially dependent properties could be conducted via scanning probe microscopy at low temperatures. Using electrostatic force microscopy could reveal the wavelength of any charge density wave state that exists in the system. On the other hand, using a magnetic tip and performing magnetic force microscopy could uncover if the nematicity was related to a spin density wave as well as uncovering any other long range magnetic order in the system.

Upon further lowering the temperature to 30 mK, we found that the (111) LAO/STO interface played host to superconductivity. Furthermore, the interface exhibited hysteretic magnetoresistance, showing that, similar to the (001) interface, ferromagnetism coexisted with superconductivity at the (111) interface. Additionally, just like in the (001) LAO/STO heterostructures, the superconductivity in the (111) LAO/STO was tunable via V_g , which yielded a non-monotonic dependence of I_C and $H_{c\perp}$, and exhibited many other similar properties. For instance, the coherence length as well as the thickness of the 2DCG were both similar to length scales found in the (001) LAO/STO. Most importantly, the low temperature properties also exhibited anisotropic behavior with respect to the in-plane crystal directions, even in the superconducting state, and this anisotropy scaled with V_g . Again, the anisotropy was largest at negative V_g and for samples with the lowest oxygen vacancy concentrations. This was very interesting, because it may indicate that the superconductivity at the (111) LAO/STO interface has an unconventional, non *s*-wave, symmetry in the superconducting gap. Beyond scanning probe microscopy techniques, the nature of the superconducting state state could be probed by more conventional mesoscopic samples. For instance, using our home built ion mill, it is possible to create rings that are made from the LAO/STO heterostructure. Each arm of the ring could be locally gated into the insulating state with top gate potential creating a SQUID with which the current-phase relation of the superconducting state could be measured.

We also discovered that the (111) LAO/STO heterostructures manifested an intriguing memory effect that froze different electronic properties into the samples based on what V_g was applied when the samples were cooled from 4.4 K to 30 mK. We found that the memory effect changed not only the normal state resistance of the 2DCG, but also changed every property of the superconducting state, including the dependence of I_C , H_C , and T_C on V_g . Through careful measurement of the R_L vs V_g at different temperatures we were able to determine that this memory effect onsets at $T \approx 600$ mK, but was not the driving mechanism behind it. Again, low temperature scanning probe microscopy would be a perfect tool for examining these ultra low temperature properties. In this case magnetic force microscopy could be employed in the superconducting state to examine the vortices in the system as they would be elongated along the nematic easy axis. One such microscope is currently finishing its development stage in our group, so we may soon be able to directly examine the nature of the nematic state at the (111) LAO/STO interface.

References

- Imada, M., Fujimori, A., and Tokura, Y., 'Metal -insulator transistions, "Rev. Mod. Phys. 70, 1039-1262 (1998).
- [2] H. Y. Hwang, Y. Iwasa, M. Kawasaki, B. Keimer, N. Nagaosa and Y. Tokura, 'Emergent phenomena at oxide interfaces,' *Nature Materials* 11, 103 (2012).
- [3] Ohtomo, A., Hwang, H. Y., A high-mobility electron gas at the LaAlO₃/SrTiO₃ heterointerface. *Nature* 427, 423-426 (2004).
- [4] Evgeny Y. Tsymbal, Elbio R. A. Dagotto, Chang-Beom Eom, Ramamoorthy Ramesh. *Multifunctional Oxide Heterostructures*. (Oxford University Press, USA, 2012).
- [5] Thiel, S., Hammerl, G., Schmehl, A., Schneider, C. W. and Mannhart J. Tunable Quasi-Two-Dimensional Electron Gases in Oxide Heterostructures. *Science* 313, 1942-1945 (2006).
- [6] Reyren, N., Thiel, S., Caviglia, A. D., Fitting Kourkoutis, L., Hammerl,G., Richter,C., Schneider,C. W., Kopp, T., Rëtschi, A.-S., Jaccard, D., Gabay, M., Muller, D. A., Triscone, J.-M. and Mannhart, J. Superconducting Interfaces Between Insulating Oxides. *Science* **317**, 1196-1199 (2007).
- [7] Caviglia, A. D., Gariglio, S., Reyren, N., Jaccard, D., Schneider, T., Gabay, M., Thiel, S., Hammerl, G., Mannhart, J. and Triscone J.-M. Electric field control of the LaAlO₃/SrTiO₃ interface ground state. *Nature* **456**, 624-627 (2008).
- [8] A. Brinkman, M. Huijben, M. van Zalk, J. Huijben, U. Zeitler, J. C. Maan, W. G. van der Weil, G. Rijnders, D. H. A. Blank and H. Hilgenkamp, 'Magnetic effects at the interface between non-magnetic oxides,' *Nature Materials* 6, 493 (2007).
- [9] M. Ben Shalom, C. W. Tai, Y. Lereah, M. Sachs, E. Levy, D. Rakhmilevitch, A. Palevski, Y. Dagan, 'Anisotropic magnetotransport at the LaAlO₃/SrTiO₃ interface,' Phys. Rev B 80, 140403 (2009).

- [10] Ariando, X. Wang, G. Baskaran, Z. Q. Liu, J. Huijben, J. B. Yi, A. Annadi, A. Roy Barman, A. Rusydi, S. Dhar, Y. P. Feng, J. Ding, H. Hilgenkamp, and T. Venkatesan, "Electronic phase separation at the LaAlO₃/SrTiO₃ interface," *Nat. Commun.* 2 1192 (2011).
- [11] N. Pavlenko, T. Kopp, E. Y. Tsymbal, G. A. Sawatzky, and J. Mannhart, "Magnetic and superconducting phases at the LaAlO₃/SrTiO₃ interface: The role of interfacial Ti_{3d} electrons" *Phys. Rev. B* 85, 020407(R) (2012).
- [12] S. Banerjee, O. Erten & M. Randeria, "Electronic phase separation at the LaAlO₃/SrTiO₃ interface," Nat. Phys. 9, 626 (2013).
- [13] A. Joshua, J. Ruhman, S. Pecker, E. Altman, and S. Ilani, "Gate-tunable polarized phase of two-dimensional electrons at the LaAlO₃/SrTiO₃ interface," *PNAS* **110**, 9633 (2013).
- [14] C. Cen, S. Thiel, G. Hammerl, C. W. Schneider, K. E. Andersen, C. S. Hellberg, J. Mannhart and J. Levy, 'Nanoscale control of an interfacial metal-insulator transition at room temperature,' *Nature Materials* 7, 298 (2008).
- [15] T. Schneider, A. D. Caviglia, S. Gariglio, N. Reyren, and J.-M. Triscone, 'Electrostatically-tuned superconductor-metal-insulator quantum transition at the LaAlO₃/SrTiO₃ interface *Phys. Rev. B* **79**, 184502 (2009).
- [16] K. Gopinadhan, A. Annadi, Y. Kim, A. Srivastava, B. Kumar, J. Chen, J. M. D. Coey, Ariando, and T. Venkatesan, "Gate Tunable In- and Out-of-Plane Spin-Orbit Coupling and Spin-Splitting Anisotropy at LaAlO₃/SrTiO₃ (110) Interface," Adv. Electron. Mater. 1, 1500114 (2015).
- [17] A. D. Caviglia, M. Gabay, S. Gariglio, N. Reyren, C. Cancellieri, and J.-M. Triscone, 'Tunable Rashba Spin-Orbit Interaction at Oxide Interfaces,' *Phys. Rev. Lett.* 104, 126803 (2010).
- [18] M. Ben Shalom, M. Sachs, D. Rakhmilevitch, A. Palevski, Y. Dagan, 'Tuning Spin-Orbit Coupling and Superconductivity at the SrTiO₃/LaAlO₃ Interface: A Magnetotransport Study,' *Phys. Rev. Lett.* **104**, 126802 (2010).
- [19] A. D. Caviglia, M. Gabay, S. Gariglio, N. Reyren, C. Cancellieri, and J.-M. Triscone, 'Tunable Rashba Spin-Orbit Interaction at Oxide Interfaces,' *Phys. Rev. Lett.* 104, 126803 (2010).

- [20] Dikin, D. A., Mehta, M., Bark, C. W., Folkman, C. M., Eom, C. B. and Chandrasekhar, V. 'Coexistence of superconductivity and ferromagnetism in two dimensions,' *Phys. Rev. Lett* **107**, 056802 (2011).
- [21] Bert, J. A., Kalisky, B., Bell, C., Kim, M., Hikita, Y., Hwang, H. Y. and Moler, K. A. Direct imaging of the coexistence of ferromagnetism and superconductivity at the LaAlO3/SrTiO3 interface. *Nat. Phys.* 7, 767-771 (2011).
- [22] Li, L., Richter, C., Mannhart, J. and Ashoori, R. C. Coexistence of magnetic order and two-dimensional superconductivity at LaAlO₃/SrTiO₃ interfaces. *Nat. Phys.* 7, 762-766 (2011).
- [23] M.M. Mehta, D.A. Dikin, C.W. Bark, S. Ryu, C.M. Folkman, C.B. Eom, and V. Chandrasekhar, "Evidence for charge-vortex duality at the LaAlO₃/SrTiO₃ interface" *Nat. Commun.* **3** 1959 (2012).
- [24] G. Herranz, F. Snchez, N. Dix, M. Scigaj, and J. Fontcuberta, "High mobility conduction at (110) and (111) LaAlO₃/SrTiO₃ interfaces" Sci Rep. 2, 758 (2012).
- [25] A. Annadi, Q. Zhang, X. Renshaw Wang, N. Tuzla, K. Gopinadhan, W. M. Lu, A. R. Barman, Z. Q. Liu, A. Srivastava, S. Saha, Y. L. Zhao, S. W. Zeng, S. Dhar, E. Olsson, B. Gu, S. Yunoki, S. Maekawa, H. Hilgenkamp, T. Venkatesan and Ariando, "Anisotropic two-dimensional electron gas at the LaAlO₃/SrTiO₃ (110) interface" Nat. Commun. 4, 1838 (2013).
- [26] T.C. Rodel, C. Bareille, F. Fortuna, C. Baumier, F. Bertran, P. Le Fevre, M. Gabay, O. Hijano Cubelos, M. J. Rozenberg, T. Maroutian, P. Lecoeur, & A. F. Santander-Syro, "Orientational Tuning of the Fermi Sea of Confined Electrons at the SrTiO₃(110) and (111) Surfaces," *Phys. Rev. Applied* 1, 051002 (2014).
- [27] S. McKeown Walker, A. de la Torre, F. Y. Bruno, A. Tamai, T.K. Kim, M. Hoesch, M. Shi, M. S. Bahramy, P. D. C. King, and F. Baumberger, "Control of a twodimensional electron gas on SrTiO₃(111) by atomic oxygen," *Phys.Rev.Lett.* **113**, 177601 (2014).
- [28] D. Doennig, W. E. Pickett and Rossitza Pentcheva, "Massive Symmetry Breaking in LaAlO₃/SrTiO₃ (111) Quantum Wells: A Three-Orbital Strongly Correlated Generalization of Graphene" *Phys.Rev.Lett.* **111**, 126804 (2013).
- [29] S. K. Davis, Z. Huang, K. Han, Ariando, T. Venkatesan, V. Chandrasekhar, "Magnetoresistance in the superconducting state at the (111) LaAlO₃/SrTiO₃ interface" arXiv:1707.03029 (2017).

- [30] S. K. Davis, Z. Huang, K. Han, Ariando, T. Venkatesan, V. Chandrasekhar, "Anisotropic Superconductivity and Frozen Electronic States at the (111) LaAlO₃/SrTiO₃ Interface," arXiv:1704.01203 (2017).
- [31] S. K. Davis, Z. Huang, K. Han, Ariando, T. Venkatesan, V. Chandrasekhar, "Anisotropic, multi-carrier transport at the (111) LaAlO₃/SrTiO₃ interface," *Phys. Rev. B* **95**, 035127 (2017).
- [32] S. K. Davis, Z. Huang, K. Han, Ariando, T. Venkatesan, V. Chandrasekhar, "Electrical transport anisotropy controlled by oxygen vacancy concentration in (111) LaAlO₃/SrTiO₃ interface structures," Adv. Mater. Interfaces 1600830, (2017).
- [33] S. K. Davis, Z. Huang, K. Han, Ariando, T. Venkatesan, V. Chandrasekhar, "Signatures of Electronic Nematicity in (111) LaAlO₃/SrTiO₃ Interfaces," arXiv:1708.04809 (2017)
- [34] Kim, M. G. et al., 'Character of the structural and magnetic phase transitions in the parent and electron-doped BaFe₂As₂ compounds,' *Phys. Rev. B.* 83, 134522 (2011).
- [35] Kasahara, S. *et al.*, 'Electronic nematicity above the structural and superconducting transition in BaFe₂(As_{1-x}P_x)₂,' *Nature* **486**, 382-385 (2012).
- [36] Yi, M. et al., 'Symmetry-breaking orbital anisotropy observed for detwinned $Ba(Fe_{1?x}Co_x)_2As_2$ above the spin density wave transition,' Proc. Natl Acad. Sci. USA 108, 6878-6883 (2011).
- [37] Cooper,K. B., Lilly, M. P., Eisenstein, J. P., Pfeiffer, L. N., and West, K. W., 'Onset of anisotropic transport of two-dimensional electrons in high Landau levels: Possible isotropic-to-nematic liquid-crystal phase transition,' *Phys. Rev. B* 65,241313(R) (2002).
- [38] Nagai, Y., Nakamura, H., and Machida, M. 'Rotational isotropy breaking as proof for spin-polarized Cooper pairs in the topological superconductor $Cu_xBi_2Se_3$,' *Phys. Rev. B* **86**, 094507 (2012).
- [39] P. K. Rout, I. Agireen, E. Maniv, M. Goldstein, and Y. Dagan1, Phys. Rev. B 95, 241107(R) (2017).
- [40] A.M.R.V.L. Monteiro, D.J. Groenendijk, I. Groen, J. de Bruijckere, R. Gaudenzi,1 H.S.J. van der Zant, and A.D. Caviglia, *Phys. Rev. B* 96, 020504(R) (2017).

- [41] K. Alex Muller, W. Berlinger, and E. Tosatti, 'Indication for a novel phase in the quantum paraelectric regime of SrTiO₃,' Z. Phys. B 84, 277-283 (1991).
- [42] C. S. Koonce, Marvin Cohen, J. F. Schooley, W. R. Hosler, and E. R. Pfeiffer, 'Superconducting Transition Temperatures of Semiconducting SrTiO₃,' *Phys. Rev.* 163, 380 (1967).
- [43] J. F. Schooley, W. R. Hosler, and Marvin L. Cohen, Superconductivity in Semiconducting SrTiO₃, *Phys. Rev. Lett.* **12**, 474 (1964).
- [44] H. P. R. Frederikse, W. R. Thurber, and W. R. Hosler, Electronic Transport in Strontium Titanate, *Phys. Rev.* 134, A442 (1964).
- [45] O.M.NES, K.A. MULLER, T. SUZUKI, F. FOSSHE, 'Elastic Anomalies in the Quantum Paraelectric Regime of SrTiO₃,' *Europhys. Lett.*, **19** (5), pp. 397-402 (1992).
- [46] MARVIN L. COHEN, The Existence of a Superconducting State in Semiconductors, *Rev. Mod. Phys.* 36, 240 (1964).
- [47] A. H. Kahn and A. J. Leyendecker, Electronic Energy Bands in Strontium Titanate, *Phys. Rev.* 135, A1321 (1964).
- [48] L. F. Mattheiss, Energy Bands for KNiF₃, SrTiO₃, KMoO₃, and KTaO₃, Phys. Rev. B 6, 4718 (1972).
- [49] L. F. Mattheiss, 'Effects of the 110° K Phase Transition on the Srtio₃ Conduction Bands,' Phys. Rev. B 6, 4740 (1972).
- [50] M. Cardona, *Phys. Rev.* **140**, A651 (1965).
- [51] S. K. Kurtz, in Proceedings of the International Meeting on Ferroelectricity, edited by V. Dvolak, A. Fouskova, and P. Glogar (Institute of Physics, Czechoslovak Academy of Sciences, Prague, 1966).
- [52] William Shockley, On the Surface States Associated with a Periodic Potential, Phys. Rev. 56, 317 (1939).
- [53] Igor Tamm, On the possible bound states of electrons on a crystal surface, Phys. Z. Soviet Union 1, 733 (1932).
- [54] Jules D. Levine and Peter Mark, Theory and Observation of Intrinsic Surface States on Ionic Crystals, *Phys. Rev.* 144, 751 (1966).

- [55] E. Heifets, R. I. Eglitis, E. A. Kotomin, and G. Borstel, 'Ab initio Calculations for SrTiO3 (100) Surface Structure,' AIP Conference Proceedings 626, 285 (2002).
- [56] Douglas H. Lowndes, X.Y. Zheng, Shen Zhu, J. D. Budai and R. J. Warmack, Appl. Phys. Lett. 61, 852 (1992).
- [57] W. J. Lin, T. Y. Tseng, H. B. Lu, S. L. Tu, S. J. Yang and I. N. Lin, J. Appl. Phys. 77, 6466 (1995).
- [58] J. Mannhart and D. G. Schlom, Oxide Interfaces: An Opportunity for Electronics, Science 327, 1607 (2010).
- [59] Andrei V. Bandura, Robert A. Evarestov and Yuri F. Zhukovskii, Energetic stability and photocatalytic activity of SrTiO₃ nanowires: ab initio simulations, *RSC Adv.*, 5, 24115 (2015).
- [60] W. Meevasana, P. D. C. King, R. H. He, S.-K. Mo, M. Hashimoto, A. Tamai, P. Songsiriritthigul, F. Baumberger, and Z.-X. Shen, *Nat. Mater.* 10, 114 (2011).
- [61] A.F. Santander-Syro, O. Copie, T. Kondo, F. Fortuna, S. Pailhes, R. Weht, X. G. Qiu, F. Bertran, A. Nicolaou, A. Taleb-Ibrahimi, P. Le Fevre, G. Herranz, M. Bibes, N. Reyren, Y. Apertet, P. Lecoeur, A. Barthelemy, and M. J. Rozenberg, *Nature (London)* 469, 189 (2011).
- [62] A. F. Santander-Syro, F. Fortuna, C. Bareille, T. C. Rodel, G. Landolt, N. C. Plumb, J. H. Dil and M. Radovic, 'Giant spin splitting of the two-dimensional electron gas at the surface of SrTiO₃,' *Nat. Mat.* **13**, 1085 (2014).
- [63] S. McKeown Walker *et al.*, 'Absence of giant spin splitting in the two-dimensional electron liquid at the surface of SrTiO3 (001),' *PHYS. REV B* **93**, 245143 (2016)
- [64] P. D. C. King, S. McKeown Walker, A. Tamai, A. de la Torre, T. Eknapakul, P. Buaphet, S.-K. Mo, W. Meevasana, M. S. Bahramy, and F. Baumberger, *Nat. Commun.* 5, 3414 (2014).
- [65] K. Alex Mullter, H. Burkard, SrTiO₃: An intrinsic quantum paraelectric below 4 K, Phys. Rev. B 19, 7 (1979).
- [66] J. Hemberger, M. Nicklas, R. Viana, P. Lunkenheimer, A. Loidl, and R. Bohmer, 'Quantum paraelectric and induced ferroelectric states in SrTiO₃,' J. Phys. Condens. Matter 8 (1996).

- [67] R. C. Neville, B. Hoeneisen, and C. A. Mead, 'Permittivity of Strontium Titanate,' Journal of Applied Physics 43, 2124 (1972).
- [68] Farrel W. Lytle, 'X-Ray Diffractometry of Low-Temperature Phase Transformations in Strontium Titanate,' *Journal of Applied Physics* 35, 2212 (1964).
- [69] H. Unoki and Y. Sakudo, J Phys. Soc. Japan 23, 546 (1967).
- [70] P. A. Fleury, J. F. Scott, and J. M. Worlock, 'SOFT PHONON MODES AND THE 110°K PHASE TRANSITION IN SrTiO₃,' *Phys. Rev. B* 21, 1 (1968).
- [71] R. Viana, P. Lunkenheimer, J. Hemberger, R. Bohmer, and A. Loidl, 'Dielectric spectroscopy in SrTiO₃,' *Phys. Rev. B* 50, 1 (1994).
- [72] A. Buckley, J. P. Rivera, E. K. H. Salje, 'Twin structures in tetragonal SrTiO₃. The ferroelastic phase transition and the formation of needle domains,' *Journal of Applied Physics* 86, 1653 (1999).
- [73] B, Hehlen, A. Perou, E. Courtens, and R. Vacher, 'Observation of a Doublet in the Quasielastic Central Peak of Quantum-Paraelectric SrTiO₃, *Phys. Rev. B* **75**, 12 (1995).
- [74] R. Blinc, B. Zalar, V. V. Laguta, and M. Itoh, 'Order Disorder Component in the Phase Transition Mechanism of ¹80 Enriched Strontium Titanate,' *PRL* 94, 147601 (2005).
- [75] M. Honig, J. A. Sulpizi, J. Drori, A. Joshua, E. Zeldov and S. Ilani, 'Local electrostatic imaging of striped domain order in LaAlO₃/SrTiO₃,' *Nat. Mat.* **12**, 1112-1118 (2013).
- [76] Harsan Ma, H.J., et al., 'Local Electrical Imaging of Tetragonal Domains and Field-Induced Ferroelectric Twin Walls in Conducting SrTiO₃,' Phys. Rev. Lett. 116, 257601 (2016).
- [77] J. Mannhart, D.H.A. Blank, H.Y. Hwang, A.J. Millis, and J.-M. Triscone, 'Two-Dimensional Electron Gases at Oxide Interfaces,' *MRS BULLETIN*, **33**, 1027 (2008).
- [78] M. Sing et al., Profiling the Interface Electron Gas of LaAlO₃/SrTiO₃ Heterostructures with Hard X-Ray Photoelectron Spectroscopy, Phys. Rev. Lett., 102, 176805 (2009).

- [79] G. Herranz et al., High Mobility in LaAlO₃/SrTiO₃ Heterostructures: Origin, Dimensionality, and Perspectives, Phys. Rev. Lett., 98, 216803 (2007).
- [80] S Gariglio, A Fte and J-M Triscone, Electron confinement at the LaAlO₃/SrTiO₃ interface, J. Phys.: Condens. Matter 27, 283201 (2015).
- [81] M. Basletic *et al.*, Mapping the spatial distribution of charge carriers in LaAlO₃/SrTiO₃ heterostructures, *Nature Materials* 7, 621 (2008).
- [82] Massimiliano Stengel, First-Principles Modeling of Electrostatically Doped Perovskite Systems, *Phys. Rev. Lett.*, **106**, 136803 (2011).
- [83] R. Pentcheva and W.E. Pickett, 'Correlation-Driven Charge Order at the Interface between a Mott and a Band Insulator,' *Phys. Rev. Lett.*, **99**, 016802 (2007).
- [84] R. Pentcheva and W.E. Pickett, 'Ionic relaxation contribution to the electronic reconstruction at the n-type LaAlO₃/SrTiO₃ interface,' *Phys. Rev. B*, **78**, 205106 (2008).
- [85] Karolina Janicka, Julian P. Velev, and Evgeny Y. Tsymbal, 'Quantum Nature of Two-Dimensional Electron Gas Confinement at LaAlO₃/SrTiO₃ Interfaces,' *Phys. Rev. Lett.*, **102**, 106803 (2009).
- [86] Michaeli, K., Potter, A. C., and Lee, P. A. Phys. Rev. Lett. 108, 117003 (2012).
- [87] N C Bristowe, Philippe Ghosez, P. B. Littlewood, and Emilio Artacho, 'The origin of two-dimensional electron gases at oxide interfaces: insights from theory,' J. Phys.: Condens. Matter 26, (2014)
- [88] K. Yoshimatsu, R. Yasuhara, H. Kumigashira, and M. Oshima, 'Origin of Metallic States at the Heterointerface between the Band Insulators,' LaAlO₃ and SrTiO₃, *Phys. Rev. Lett.* **101**, 026802 (2008).
- [89] Z. Q. Liu, C. J. Li, W. M. Lu, X. H. Huang, Z. Huang, S. W. Zeng, X. P. Qiu, L. S. Huang, A. Annadi, J. S. Chen, J. M. D. Coey, T. Venkatesan, and Ariando, 'Origin of the Two-Dimensional Electron Gas at LaAlO₃/SrTiO₃ Interfaces: The Role of Oxygen Vacancies and Electronic Reconstruction,' *Phys. Rev. X* 3, 021010 (2013).
- [90] Alexey Kalabukhov, Robert Gunnarsson, Johan Börjesson, Eva Olsson, Tord Claeson, and Dag Winkler, Effect of oxygen vacancies in the SrTiO₃ substrate on the electrical properties of the LaAlO₃?SrTiO₃ interface. *Phys. Rev. B* **75**, 121404(R) (2007).
- [91] W. Siemons, G. Koster, H. Yamamoto, W. A. Harrison, G. Lucovsky, T. H. Geballe, D. H. A. Blank, M. R. Beasley, 'Origin of Charge Density at LaAlO₃ on SrTiO₃ Heterointerfaces: Possibility of Intrinsic Doping,' *Phys. Rev Lett* **98**, 196802 (2007).
- [92] Z. Q. Liu, D. P. Leusink, X. Wang, W. M. Lu, K. Gopinadhan, A. Annadi, Y. L. Zhao, X. H. Huang, A. Srivastava, S. Dhar, T. Venkatesan, and Ariando, Metal-Insulator Transition in SrTiO3 x Thin Films Induced by Frozen-Out Carriers, *Phys. Rev. Lett.* **107**, 146802 (2011).
- [93] O. N. Tufte and P. W. Chapman. Electron Mobility in Semiconducting Strontium Titanate. Phys. Rev. 155, 796?802 (1967).
- [94] Borzi, R. A. et al., 'Formation of a nematic fluid at high fields in Sr₃Ru₂O₇,' Science 315, 214-217 (2007).
- [95] Fu, L. 'Odd-parity topological superconductor with nematic order: application to $Cu_xBi_2Se_3$,' *Phys. Rev. B* **90**, 100509(R) (2014).
- [96] J. Wu, A. T. Bollinger, X. He, and I. Bozovic, 'Spontaneous breaking of rotational symmetry in copper oxide superconductors,' *Nature* 547, 432?435 (2017).
- [97] J. P. Eisenstein, L. N. Pfeiffer, and K. W. West, *Phys. Rev. B* 50, 1760 (1994).
- [98] J. P. Eisenstein, L. N. Pfeiffer, and K. W. West, 'Negative Compressibility of Interacting Two-Dimensional Electron and Quasiparticle Gases,' *Phys.Rev.Lett.* 68, 5 (1992).
- [99] L. J. Van der Pauw, 'DETERMINATION OF RESISTIVITY TENSOR AND HALL TENSOR OF ANISOTROPIC CONDUCTORS,' *PhilipsRes.Repts* 16,187-195, (1961).
- [100] Y. C. Akgoz and G. A. Saunders, 'Space-time symmetry restrictions on the form of transport tensors: I. Galvanomagnetic effects,' J. Phys. C: Solid State Phys., Vol. 8, (1975).
- [101] Y. C. Akgoz and G. A. Saunders, 'Space-time symmetry restrictions on the form of transport tensors. II. Thermomagnetic effects,' J. Phys. C: Solid State Phys., Vol. 8, (1975).
- [102] Charles Kittel, 'Quantum Theory of Solids,' Wiley; 2 edition (April 2, 1987).

- [103] William Jones and Norman H. March, 'Theoretical Solid State Physics, Vol. 2: Non-Equilibrium and Disorder (Non-Equilibrium & Disorder),' Dover Publications (September 1, 1985).
- [104] Walter A. Harrison, 'Solid State Theory (Dover Books on Physics),' Dover Publications; 1st THUS edition (May 1, 1980).
- [105] P. Brinks, W. Siemons, J. E. Kleibeuker, G. Koster, G. Rijnders, & M. Huijben et al., Appl. Phys. Lett. 98, 242904 (2011).
- [106] Y. Frenkel, N. Haham, Y. Shperber, C. Bell, Y.Xie, Z. Chen, Y. Hikita, H. Y. Hwang, and B. Kalisky, ACS Appl. Mater. Interfaces 8, 12514 (2016).
- [107] Boudjada, N., Wachtel, G., and Paramekanti, A., 'Magnetic and Nematic Orders of the Two-Dimensional Electron Gas at the Oxide (111) Surfaces and Interfaces,' arXiv 1705.10795 (2017).
- [108] M. S. Scheurer, D. F. Agterberg, and J. Schmalian, 'Selection rules for Cooper pairing in two-dimensional interfaces and sheets,' NPJ: Quantum Materials 2:9, (2017).
- [109] Laurence D. Marks, Ann N. Chiaramonti, Fabien Tran and Peter Blaha, 'The Small Unit Cell Reconstructions of SrTiO₃ (111),' Surface Science 603, 2179-2187, 2009
- [110] Jaewan Chang, Yoon-Seok Park, and Sang-Koog Kim, 'Atomically flat singleterminated SrTiO₃ (111) surface,' Appl. Phys. Lett. 92, 152910 (2008)
- [111] A. Biswas, P. B. Rossen, C.-H. Yang, W. Siemons, M.-H. Jung, I. K. Yang, R. Ramesh, and Y. H. Jeong, 'Universal Ti-rich termination of atomically flat SrTiO₃ (001), (110), and (111) surfaces,' *Appl. Phys. Lett.* **98**, 051904 (2011).
- [112] Y. Mukunoki, N. Nakagawa, T. Susaki, and H. Y. Hwang, 'Atomically flat (110) SrTiO₃ and heteroepitaxy,' Appl. Phys. Lett. 86, 171908 (2005).
- [113] J. L. Blok, X. Wan, G. Koster, D. H. A. Blank, and G. Rijnders, 'Epitaxial oxide growth on polar (111) surfaces,' Appl. Phys. Lett. 99, 151917 (2011)
- [114] J. W. Park, S. H. Baek, C. W. Bark, M. D. Biegalski, and C. B. Eom, 'Quasi-singlecrystal (001) SrTiO₃ templates on Si,' Appl. Phys. Lett. 95, 061902 (2009).
- [115] M. Saghayezhian, Lina Chen, Gaomin Wang, Hangwen Guo, E. W. Plummer, and Jiandi Zhang, 'Polar compensation at the surface of SrTiO₃(111),' *Phys. Rev. B* 93, 125408 (2016).

- [116] D. Xiao, W. Zhu, Y. Ran, N. Nagaosa, and S. Okamoto, *Nature Commun.* 2, 596 (2011).
- [117] K. Sun, Z. Gu, H. Katsura, and S. Das Sarma, *Phys. Rev. Lett.* **106**, 236803 (2011).
- [118] C. Wu, D. Bergman, L. Balents, and S. Das Sarma, Phys. Rev. Lett. 99, 070401 (2007).
- [119] Jonghwa Eom, Ph.D. Thesis, Northwestern University (1998).
- [120] Chen-jung Chien, Ph.D. Thesis, Northwestern University (1998).
- [121] Jose Aumentado, Ph.D. Thesis, Northwestern University (2000).
- [122] Zhigang Jiang, Ph.D. Thesis, Northwestern University (2005).
- [123] Zhengfan Zhang, Ph.D. Thesis, Northwestern University (2006).
- [124] Paul Cadden-Zimansky, Ph.D. Thesis, Northwestern University (2008).
- [125] Manan Mehta, Ph.D. Thesis, Northwestern University (2015).
- [126] Howard M. Smith and A. F. Turner, Vacuum Deposited Thin Films Using a Ruby Laser, Applied Optics 4, 147-148 (1965).
- [127] Douglas H. Lowndes, D. B. Geohegan, A. A. Puretzky, D. P. Norton, C. M. Rouleau, Synthesis of Novel Thin-Film Materials by Pulsed Laser Deposition, *Science* 273, 898-903 (1996).
- [128] Z.Q. Liu, Z. Huang, W.M. Lu, K. Gopinadhan, X. Wang, A. Annadi, T. Venkatesan, and Ariando, Atomically Flat Interface between a Single-Terminated LaAlO3 Substrate and SrTiO3 Thin Film Is Insulating, *AIP Adv.* 2, 012147 (2012).
- [129] Micro Chem, 'NanoTM PMMA and Copolymer,' *Microchem.com* (2006).
- [130] South Bay Technology, inc., 'Fundamentals of the Kaufman Ion Source for the IBS/e and Operational Notes,' southbaytech.com, (2009).
- [131] Wayne Stauss and Todd Lizotte, 'Ion Beam Etch System Diagram,' microfabnh.com (2010).
- [132] D. W. Reagor and V. Y. Butko, Nat. Mat. Lett. 4, 593 (2005).

- [133] D. Kan, T. Terashima, R. Kanda, A. Masuno, K. Tanaka, S. Chu, H. Kan, A. Ishizumi, Y. Kanemitsu, Y. Shi- makawa, et al., *Nat Mater* 4, 816 (2005).
- [134] D. Kan, O. Sakata, S. Kimura, M. Takano, and Y. Shi- makawa, Japanese Journal of Applied Physics 46, L471 (2007).
- [135] H. Gross, N. Bansal, Y. Kim, and S. Oh, Journal of Applied Physics 110, 073704 (2011)
- [136] Photonic Science LTD, 'Photonic Science Desktop Systems for LAUE real-time Crystal Orientation and Characterization,' photonic-science.co.uk, (2017).
- [137] Bertram Eugene Warren, 'X-ray Diffraction,' Dover Publications; Reprint edition (June 1, 1990).
- [138] 'Crystal orientation : Inel Laue Diffraction System,' Laue Diffraction, INEL inc. (2016).
- [139] Kira, M., Koch, S. W. (2011). Semiconductor Quantum Optics. Cambridge University Press. ISBN 978-0521875097.
- [140] Leonelli, R. & Brebner, J. L., 'Time-resolved spectroscopy of the visible emission band in strontium titanate.' *Phys. Rev. B* 33, 8649-8656 (1986).
- [141] Hasegawa, T., Shirai, M. & Tanaka, K., 'Localizing nature of photo-excited states in SrTiO₃,' J. Lumin. 87-89, 1217-1219 (2000).
 ? Emmanuelle Orhan et al., 'Origin of photoluminescence in SrTiO₃: a combined experimental and theoretical study,' Journal of Solid State Chemistry 177 (2004) 3879?3885
- [142] Alexey Kalabukhov, Robert Gunnarsson, Johan Borjesson, Eva Olsson, Tord Claeson, and Dag Winkler, 'Effect of oxygen vacancies in the SrTiO3 substrate on the electrical properties of the LaAlO₃/SrTiO₃ interface,' *Phys. Rev. B* **75**, 121404(R) (2007).
- [143] G. L. Yu, et al., 'Interaction phenomena in graphene seen through quantum capacitance,' PNAS 110, 9 (2013).
- [144] Nan Ma and Debdeep Jena, 'Carrier statistics and quantum capacitance effects on mobility extraction in two-dimensional crystal semiconductor field-effect transistors,' 2D Mater. 2 015003, (2015).

- [145] L. Li, C. Richter, S. Paetel, T. Kopp, J. Mannhart, R. C. Ashoori Science 332, 825 (2011).
- [146] N.W. Ashcroft and N.D. Mermin, *Solid State Physics*, Fort Worth: Harcourt [1976].
- [147] V. Bal, Z. Huang, K. Han, Ariando, T. Venkatesan, V. Chandrasekhar, "Electrostatic tuning of magnetism at the conducting (111) (La₀.3Sr₀.7)(Al₀.65Ta₀.35)/SrTiO3 interface," Appl. Phys Lett. 111, 081604 (2017)
- [148] Ludi Miao, Renzhong Du, Yuewei Yin, and Qi Li, "Anisotropic magneto-transport properties of electron gases at the SrTiO₃ (111) and (110) surfaces," Appl. Phys Lett. 109, 261604 (2016)
- [149] M. Tinkham, Introduction to Superconductivity (McGraw-Hill Inc., New York, 1996), 2nd edition, p119.
- [150] J. Wu, A. T. Bollinger, X. He, and I. Bozovic, 'Spontaneous breaking of rotational symmetry in copper oxide superconductors,' *Nature* 547, 432?435 (2017).
- [151] Khalsa, G., Lee, B., and MacDonald, A. H., 'Theory of t_{2g} electron-gas Rashba interactions.,' *Phys. Rev. B* 88, 041302(R) (2013).
- [152] J Sidoruk, J. Leist, H. Gibhardt, M. Meven, K. Hradil, and G. Eckold, 'Quantitative determination of the domain distribution in SrTiO₃- competing effects of applied electric field and mechanical stress,' *J.Phys:Condens. Matter* 22, 235903 (2010).
- [153] van Harlingen, D.J. 'Phase-sensitive tests of the symmetry of the pairing state in the high-temperature superconductors? Evidence for dx2?y2 symmetry,' Rev. Mod. Phys. 1995, 67, 515?535.
- [154] Tsuei, C.C.; Kirtley, J.R. Pairing symmetry in cuprate superconductors. Rev. Mod. Phys. 2000, 72, 969?1016
- [155] C. Richter *et al.*, 'Interface superconductor with gap behaviour like a high-temperature superconductor,' *nature* **502**, 24 (2013).
- [156] Lukas Kuerten et al., 'In-gap features in superconducting LaAlO3-SrTiO3 interfaces observed by tunneling spectroscopy,' arXiv:1704.02122v1 (2017).
- [157] Sacepe ,B etal., 'Pseudo gap in a thin film of a conventional superconductor,' Nature Commun. 1, 140 (2010).

- [158] Feld, M., Frohlich, B., Vogt, E., Koschorreck, M. & Kohl, M., 'Observation of a pairing pseudogap in a two-dimensional Fermi gas,' *Nature* 480, 75?78 (2011).
- [159] Toshikazu Ekino *et al.*, 'd-Wave Superconductivity and s-Wave Charge Density Waves: Coexistence between Order Parameters of Different Origin and Symmetry,' *Symmetry* 3, 699-749 (2011).
- [160] V. M. Vinokur *et al.*, 'Superinsulator and quantum synchronization,' *Nature*, 452 618, (2008).
- [161] Biscaras, J. et al., 'Multiple quantum criticality in a two-dimensional superconductor,' Nat. Mater. 12, 542?548 (2013).
- [162] Rostam Moradian, and Hamzeh Mousavi, 'Validity of Anderson's theorem for swave superconductors,' arXiv:cond-mat/0505092 (2005).
- [163] Clement Collignon *et al.*, 'Superfluid density and carrier concentration across a superconducting dome: the case of SrTi1?xNbxO3,' arXiv:1703.00863v1 (2017).
- [164] Markus Thiemann *et al.*, 'Single-gap superconductivity in doped SrTiO3,' arXiv:1703.04716v1 (2017).
- [165] G. Binnig et al., 'Two-band Superconductivity in Nb-Doped SrTiO₃,' PRL 45, 1352 (1980).
- [166] Hyunwoo Jin *et al.*, 'Large linear magnetoresistance in heavily-doped Nb:SrTiO3 epitaxial thin films,' *Scientific Reports* **6**, 34295 (2016).
- [167] Venkat Chandrasekhar, Ph.D. Thesis, Yale University (1989).
- [168] P. Santhanam, Ph.D. Thesis, Yale University (1985).
- [169] Appendix A, ' T_C vs μ_0 H Analysis" Davis (2017).
- [170] P. W. Anderson, (1959), 'Theory of Dirty Superconductors,' J. Phys. Chem. Solids 11, 26-30.
- [171] S. Bose, P. Raychaudhuri, R. Banerjee, P. Vasa, & P. Ayyub, (2005), 'Mechanism of the Size Dependence of the Superconducting Transition of Nanostructured Nb,' Phys. Rev. Lett. 95, 147003.

- [172] S. Matsuo, H. Sugiura, & S. Noguchi, (1974), 'Superconducting Transition Temperature of Aluminum, Indium, and Lead Fine Particles,' J. Low Temp. Phys. 15, 5.
- [173] B. Abeles, R. W. Cohen, and G. W. Cullen, (1966), 'Enhancement of Superconductivity in Metal Films,' Phys. Rev. Lett. 17, 12.
- [174] M. Nittmann, P. Ziemann, W. Buckel, & G. Linker, (1981), 'Dependence of the Superconducting Transition Temperature of Quench-Condensed Aluminium-Films on the Oxygen Content,' Z. Phys. B -Cond. Matter 41, 205-209.
- [175] M. Mondal, M. Chand, A. Kamlapure, J. Jesudasan, V. C. Bagwe, S. Kumar, G. Saraswat, V. Tripathi,& P. Raychaudhuri, (2011), 'Phase Diagram and Upper Critical Field of Homogeneously Disordered Epitaxial 3-Dimensional NbN Films,' J. Supercond. Nov. Magn. 24, 341-344.
- [176] N. Markovic, C. Christiansen, A. M. Mack, W. H. Huber, and A. M. Goldman, (1999), 'Superconductor-insulator transition in two dimensions,' Phys. Rev. B 60, 6.
- [177] E. Shimshoni, A. Auerbach, and A. Kapitulnik, (1998), 'Transport through Quantum Melts,' Phys. Rev. Lett. 80, 15.
- [178] A. Kamlapure, T. Das, S. C. Ganguli, J. B. Parmar, S. Bhattacharyya, & P. Raychaudhuri, (2013), 'Emergence of nanoscale inhomogeneity in the superconducting state of a homogeneously disordered conventional superconductor,' Sci. Rep. 3, 2979.
- [179] P. G. De Gennes, 'Boundary Effects in Superconductors.', (1964), Rev. Mod. Phys. 36, 225.
- [180] J. W. Garland, K. H. Bennemann, and F. M. Mueller, (1968), 'Effect of Lattice Disorder on the Superconducting Transition Temperature,' Phys. Rev. Lett. 21, 1315.
- [181] H. Kotegawa, S. Kawasaki, A. Harada, Y. Kawasaki, K. Okamoto, G-q Zheng, Y. Kitaoka, E. Yamamoto, Y. Haga, Y. Onuki, K. M. Itoh, and E.E. Haller, J. Phys. Cond. Mat. 15, S2043-S2046 (2003).
- [182] W. J. Gannon, W. P. Halperin, C. Rastovski, K. J. Schlesinger, J. Hlevyack, M. R. Eskildsen, A. B. Vorontsov, J. Gavilano, U. Gasser, and G. Nagy, NJP 17, (2015)

APPENDIX A

E-beam Lithography Parameters

The procedures described in Chapter 3 are used for devices which have minimum feature sizes > 1 μ m; however, for devices with features smaller than 1 μ m electron beam lithography must be used to achieve the smaller features. The same overall process should be followed with the following substitutions.

- (1) First clean the sample as described in Chapter 3.
- (2) For e-beam lithography, use (MMA (8.5) MAA)¹ as an undercut layer if needed. MMA is spun onto the sample at 3000 rpm for 60 seconds and then baked in the oven at 140° C for 30 minutes. This yields an undercut layer that is approximately 360 nm thick. Undercut thickness can be tailored to an extent with spin speed and should be chosen to be as thin as possible while still suiting the needs of the device. For instance, if the the device to be fabricated needs to be very thick, > 360 nm, spin at a slower speed to increase the resist thickness, up to 600 nm, so that clean lift off can be accomplished.
- (3) The imaging resist used in this case is the positive e-beam resist PMMA 950 a3². PMMA is spun onto the sample at 4000 rpm for 60 seconds and then 40 minutes at 170° C. This yields a resist that is ≈ 70 nm thick.

¹Co-polymer electron beam resist, distributed by Microchem Corp., Westborough, MA

²PMMA electron beam resist, distributed by Microchem Corp., Westborough, MA. microchem.com

- (4) Exposure for e-beam lithography is handled through the Tesan SEM. Each time a new substrate, resist thickness, or line width is used you must do a dosage test to determine the electron dosage necessary for good line definition. For writing on LAO/STO it is necessary to use a lower accelerating voltage than the normal 30 kV to avoid charging. I have successfully used 5 kV and a dosage of 325 uC/cm⁻² to write 50 nm lines.
- (5) The PMMA/MMA bilayers are simultaneously developed using a mixture of 3:1 IPA:MIBK, where MIBK is short for methyl isobutyl ketone, for 55 seconds 24° C. After development is complete rinse with IPA for 30 seconds and then dry with N₂ gas.

APPENDIX B

University of Wisconsin Sample List

In addition to the samples from NUS we also received a number of samples from Chang Beom-Eom's group at the University of Wisconsin- Madison. While we did not present any of the data taken from these samples, they all showed the anisotropy observed in the NUS samples to different degrees. Except for sample W8 all of the samples had 20 uc of LAO grown on (111) STO. The deposition parameters were kept the same between the two groups.

Sample Chip Number	Post Growth Treatment	Notes
W1	None	Two Hall bars along the
		$[\bar{1}\bar{1}2]$ direction exhibited an
		incomplete superconducting
		transition to non-zero resis-
		tance. Currently in Sample
		storage
W2	None	Two Hall bars along the
		$2\overline{1}0$ direction exhibited no
		superconducting transition.
		Currently in Sample storage
W3	Oxygen annealed	4 Hall bars, 2 along each di-
		rection. This sample served
		as a test bed for the O_2
		annealing process. Cur-
		rently non-conductive and
		is in sample storage.
W4	Ar/H_2 annealed	4 Hall bars, 2 along each di-
		rection. This sample served
		as a test bed for the Ar/H_2
		annealing process. Cur-
		rently conducts through the
		bulk of the the chip and is
		located in sample storage.

Table B.1. Wisconsin Sample Numbers and Processing: The first column contains the sample chip numbers. The second column contains details on the post growth treatment conducted: none for the as-grown samples, oxygen annealed samples, UV irradiated samples, or Ar/H_2 annealed samples. Finally there is a column with notes on each sample. These notes describe the current state of the sample.

Sample Chip Number	Post Growth Treatment	Notes
W5	None	4 Hall bars, 2 along each
		direction. Shattered during
		wire bonding tests using the
		Cook clean room wirebon-
		der.
W6	Oxygen annealed	4 Hall bars, 2 along each
		direction. This sample
		served as a test bed for
		the O_2 annealing process.
		Still shows good conduction
		without shorting the 4 Hall
		bar devices.
W7	UV irradiated	4 Hall bars, 2 along each
		direction. Served as the
		UV irradiation test sam-
		ple, does not currently show
		conduction. Currently lo-
		cated in sample storage.
W8	None	4 Hall bars, 2 along each
		direction. 12 uc of LAO
		grown on (111) STO. Still
		exhibits anisotropy, but has
		a higher conductivity at
		room temperature, $R_L \approx 21$
		$ k\Omega / \Box$. Currently located in
		sample storage.

Table B.2. Wisconsin Sample Numbers and Processing, Table 2: The first column contains the sample chip numbers. The second column contains details on the post growth treatment conducted: none for the asgrown samples, oxygen annealed samples, UV irradiated samples, or Ar/H_2 annealed samples. Finally there is a column with notes on each sample. These notes describe the current state of the sample.

APPENDIX C

T_C vs μ_0 H Analysis

In perpendicular field the critical field $H_{c\perp}$ is the field required to put one superconducting flux quantum in an area ξ_{GL}^2 . $H_{c\perp}$ as a function of ξ_{GL}^2 is defined as,^{149,167,168}

(C.1)
$$H_{c\perp} = \frac{\Phi_0}{2\pi\xi_S^2(T)}$$

where the equation for the temperature dependent superconducting phase coherence length is, $^{\mathbf{149}}$

(C.2)
$$\xi_S(T) = \alpha \frac{\xi_0}{\sqrt{(1 - T/T_c)}}.$$

In this equation ξ_0 is the coherence length at zero temperature, and $\alpha=0.74$ or 0.86 for the clean and dirty limit respectively.¹⁴⁹ Therefore the dependence of $H_{c\perp}$ on T is linear, with a slope given by,^{149,167,168}

(C.3)
$$\frac{dH_{c\perp}}{dT} = -\frac{\Phi_0}{2\pi\xi_0^2 T_c},$$

where we have taken $\alpha \sim 1$. Thus by measuring the slope of the phase diagram and T_c , we could determine ξ_0 . In a parallel field, for a superconductor whose thickness d is less than ξ_S , the area is restricted by d, hence the parallel critical field is given by,^{149,167,168}

(C.4)
$$H_{c\parallel} = \frac{\sqrt{3}\Phi_0}{\pi\xi_S(T)d},$$

so that $T_c(H)$ should have a quadratic dependence on H. Using the value of ξ_0 obtained from the perpendicular field phase diagram, we fit this dependence and obtained an estimate for the thickness d of the superconductor.