STRUCTURAL AND MAGNETOTRANSPORT STUDY OF SrTiO3-8/Si

STRUCTURES GROWN BY MOLECULAR BEAM EPITAXY

By

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ABSTRACT

SrTiO₃ (STO) films were grown on p-Si (001) substrates using molecular beam epitaxy (MBE). Oxygen vacancies were introduced by controlling the Oxygen Pressure (P_{O2}) that varied from 10⁻⁸ to 10⁻⁷ torr during growth, resulting in SrTiO_{3- δ} with $\delta \sim 0.02\%$ for the lowest pressure. The single phase STO/Si films were of high crystalline quality as verified by x-ray diffraction (XRD), transmission electron microscopy (TEM), and were atomically flat as verified by atomic force microscopy (AFM), with rms roughness of less than 0.5nm measured by AFM. The thickness was measured by x-ray reflectivity. Transport measurements were performed on the STO/Si structures in a Van der Pauw configuration. We measured resistance as a function of temperature for a range of T = 3Kto 300K and as a function of an applied magnetic field, H=0 to ±9T. The resistivity decreased from 1 Ohm cm to $3x10^{-2}$ Ohm cm as the film thickness increased (3nm-60nm) at all temperatures. To identify the origin of the resistivity thickness dependence, we consider several competing effects in STO/Si such as 1.7% compressive strain induced by lattice mismatch with Si, strain and defects due to oxygen vacancies, an antiferrodistortive phase transition at 105K in bulk STO, and structural dislocations. We find that a charged space effect may explain the thickness dependence of resistivity, resulting from the interface of STO with Si and the Si doping type and concentration. The magnetic field dependence shows a reproducible trend of a positive magnetoresistance (MR) at 300K, which turns to a negative MR effect between 200K and 100K, and turns up again to a positive MR at 3K. Interestingly, at 3K, the MR starts to turn down again at high fields.

I. INTRODUCTION

The field of oxides and oxide heterostructures has received much attention lately due to their large range of electrical, magnetic, and optical properties that arise from, and can be tuned by, their electronic and crystal structures. Oxides have exhibited multiferrocity, some at 300K as seen in BiFeO₃, giant piezoelectricity in Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃, and ferroelectricity [1]. At the interface between semiconducting oxides, with SrTiO₃ and LaAlO₃ being the first and most well studied system, a 2 dimensional electron gas (2DEG) can appear which has been shown to have a non-volatile controllable metal-insulator quantum phase transition [2].

SrTiO₃ (strontium titanate, STO) in particular has proven to be very versatile in the world of oxides. STO crystallizes in a perovskite structure, shown below in figure 1.1 taken from [3], with a lattice constant of a = 3.905 Å, and has an indirect band gap of 3.2 eV. STO undergoes a structural transition from cubic to tetragonal around 105K [4]. Initially, STO was intriguing for its dielectric properties and technological applications. The dielectric constant of bulk STO is dependent on temperature and electric field, ranging from ~300 at room temperature to tens of thousands at low temperatures [5]. Since then, STO has become common in thin films due to its tunable conductivity [6]. In addition to having a close lattice match to Si as well as other oxides, STO is commercially available and has a controllable surface termination, making it popular as a substrate for oxide heterostructures [7]. The close lattice match with Si opens up the possibility of integrating oxide heterostructures onto conventional Si electronics.



Figure 1.1: ABO₃ and STO structure. (a) Schematic of the ABO₃ perovskite structure taken from Fu *et al.* [3], and (b) structure of STO taken from http://www.princeton.edu/~cavalab/tutorials/public/structures/perovskites.html.

In 2004, Hwang *et al.* discovered that a 2-dimensional electron gas (2DEG) between STO and LaAlO₃ (lanthanum aluminate, LAO) appears at a critical LAO thickness and STO termination [8]. This was an exciting discovery both in terms of basic physics but also because of the potential technological applications. The 2DEG in GaAs/AlGaAs is commercially utilized in high frequency transistors that are used for telecommunications. The discovery of a 2-dimensional electron gas (2DEG) at the STO/LAO interface has resulted in much interest and investigation into the origin and controllability of the phenomenon. Since then many groups have reproduced the results and have proposed various explanations for its origin such as an electronic reconfiguration at the interface [9, 15], or carriers due to oxygen vacancies [10 - 14].

LAO also crystallizes in a perovskite structure and has a lattice constant of 3.789 Å and a band gap of 5.6 eV. Both LAO and STO are perovskite oxides, of the form ABO₃. They are composed of alternating layers of AO and BO₂, i.e. SrO and TiO₂ for STO and LaO and AlO₂ for LAO. The 2DEG only occurs when LAO is grown on TiO₂ terminated

STO. When LAO is grown on SrO terminated STO the interface is insulating. One explanation is that the 2DEG is formed because of an electronic reconfiguration due to "polar catastrophe," [15] caused by the polar nature of LAO; the LaO layer is positively charged and the AlO₂ layer is negatively charged so LAO has a polarization that diverges with increasing thickness. In STO both the SrO and TiO₂ layers are electrically neutral so because of the increasing potential with LAO thickness, after 4 monolayers of LAO there is a shift of half an electron per unit cell down to the interface.

Since this first discovery, a 2DEG has been found between STO and other crystalline and even amorphous oxides, such as amorphous LAO, YSZ (yttria stabilized zirconia), and even amorphous STO grown on crystalline STO, [16] as well as amorphous YAIO₃ and Al_2O_3 [17]. Bulk STO is insulating, whereas Nb doped STO has conductivities of 414.93 Ohm⁻¹ cm⁻¹ at 2.00% of Nb at room temperature [18, 6]. STO has also been shown to be highly conductive by introducing oxygen vacancies through Ar bombardment or annealing [19]. Others have found a 2DEG on bare STO surfaces as well [20, 21]. These studies show that oxygen vacancies have a large effect on the conductivity of STO.

A 2DEG between STO and BiFeO₃ (bismuth ferrite, BFO), a room temperature material exhibiting more than one coupled ferroic orders, otherwise known as multiferroic, being ferroelectric ($T_C \sim 1100$ K) and antiferromagnetic ($T_N \sim 673$ K), has been theoretically predicted [22], much similar to the STO/LAO structure [23]. BFO, like STO and LAO, crystallizes in a perovskite structure and has a lattice constant of 3.93 Å, closely matched to STO. BFO is also polar, like LAO, having alternating layers of positive and negative charge, BiO¹⁺ and FeO₂¹⁻. The experimental verification of this prediction could lead to interesting applications such as gate control of the 2DEG, which has already been shown

with LAO/STO [10], by either an external electric or a magnetic field through the multiferrocicity of BFO. The initial aim of our experiments was to investigate experimentally the existence of a 2DEG at the interface of BFO and STO.

Another important factor for future device fabrication and manufacturability is the integration of these structures onto Si. It has been shown that STO can be grown epitaxially on Si as a virtual substrate for other oxide films. BFO was grown on such a structure, STO(20nm)/Si by PLD. We have shown that BFO can be grown on top of the STO/Si by molecular beam epitaxy (MBE) without breaking vacuum and that BFO retains its multiferroic properties at T = 300K. Our ability at Texas State to grow these structures by MBE without breaking vacuum and have "clean" interfaces is essential to our proposed project of investigating the interfaces. We were planning to test the proposed STO/BFO structures both on STO substrates as well as STO grown on Si by MBE. STO (001) substrates are sold commercially and they cost \sim \$60 - \$100 per 10x10 mm piece. The high price of STO combined with our established success on growing STO on Si motivated us to use MBE to grow a series of STO/Si wafers to be used as virtual substrates for future BFO growths. The thickness of 20 nm was chosen because it has been shown that STO is initially strained on Si but by 20nm thickness, the crystal is fully relaxed. The critical thickness d_{crit} for the relaxation of STO on Si is calculated by,

$$d_{crit} = \frac{\alpha_e}{2\Delta}$$

$$d_{crit} = \frac{3.905}{2*1.7} = 11.5nm$$

where α_e (α_s) is the lattice constant of the epitaxial film (substrate) and $\Delta = \frac{\alpha_e - \alpha_s}{\alpha_e}$.

During analysis of the samples, structural and magnetotransport measurements were taken on the bare Si wafers and STO substrates used, as well as on the STO/Si virtual substrates, for thoroughness and to establish a baseline with which to compare the transport and magnetotransport properties of LAO/STO/Si and BFO/STO/Si structures. Upon the electrical characterization of the STO/Si structures, we found that the resistivity as a function of temperature differed greatly from that of the bare Si wafer. Many reports on STO/Si claim low STO conductivities (sheet resistance of ~10kOhm/sq.) [24] and close to the bulk values, we didn't expect anything different on our STO/Si structures but we needed to measure them for our future experiments. Surprisingly, we measured low resistances on these samples down to 3K. From Hall measurements, we calculated the sheet carrier concentration of these structures to be on the order of 10^{14} cm⁻², which is very close in literature to the value for the 2DEG between STO and LAO, corresponding to a half electron shift per unit cell down to the interface. Since the recent reports on the 2DEG on other STO based heterostructures [16, 17], this led us to believe that a 2DEG may also exist between STO and Si!

To explore whether the high conductivity that we measured was due to a 2DEG, we decided to study this STO/Si structure much more closely. We grew more samples of STO/Si, while varying thickness and oxygen pressure, to get a more systematic study. The focus of this study is to determine the origin on this conductive behavior, whether it is a 2DEG or attributed to oxygen vacancies. This is done primarily through the transport measurements, though it was important to first analyze the structural quality of the thin films by X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron

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microscope (SEM) imaging, and transmission electron microscopy (TEM). Details on these experiments will come in the following chapters.

II. BACKGROUND

In growing and characterizing STO on Si, there are several important factors to consider. Among them are: the effect of oxygen vacancies on the electronic and lattice structure, the strain induced in STO due to a lattice mismatch with Si, oxygen vacancies, and thermal expansion, the antiferrodistortive (AFD) phase transition STO undergoes at 105K, and finally – the (potential) ferroelectric property of STO when strained.

Si has an in-plane lattice constant of 5.43 Å, whereas for STO a = 3.905 Å. The difference between these two lattice parameters is far too large to support direct growth of STO on Si. However, rotating Si by 45° with respect to STO allows STO to grow on Si. At the surface of Si, each Si atom has two dangling bonds. In reality, pairs of Si atoms at the surface dimerize and form lateral Si-Si bonds, leaving still one dangling bond per Si atom. These remaining dangling bonds form π bonds across the dimer. These dangling bond states at the surface of Si can be removed by passivating the surface with a $\frac{1}{2}$ monolayer of Sr. More details of the bonding at the interface of STO/Si are given in [25]. This gives Si a lattice constant of $a\sqrt{2} = 7.6509$ Å or $\frac{a\sqrt{2}}{2} = 3.8396$ Å with respect to the STO [001] direction; much closer to STO. These lattice parameters a = 3.8396 Å and 3.905 Å for Si and STO respectively yield a tensile strain of 1.67% of STO on Si substrate. Figure 2.1 below, taken from Eom *et al.* [26], shows the orientation of STO on Si, and figure 2.2, taken from Al-Hamadany *et al.* [27], shows how the perovskite structure behaves under compressive strain.



Figure 2.1: Schematic of STO on Si. Image taken from [26].



Figure 2.2: STO under compressive strain. (a) Schematic view showing the (001) displacement of the oxygen sub-lattice relative to the cation sub-lattice under compressive strain leading to ferroelectric distortion of SrTiO3 along the (001) direction. (b) Shows the rotation of the TiO6 polyhedral about the axis of compressive strain (001). Brown atoms are Sr, red atoms are O, and green atoms in the center are Ti. [27]

Strain can also be induced through differences in the thermal expansion coefficients (TEC) between STO and Si. Si has a well-established thermal expansion coefficient [28]. The TEC for STO has been calculated from first principles [29]. According to literature, the coefficient of thermal expansion is about an order of magnitude higher for STO than for Si at room temperature. The coefficients are temperature dependent, and decrease with decreasing temperature. The strain due to thermal expansion would be a problem for thick films, but for the thicknesses of our films the effect was not significant compared to strain due to the lattice mismatch, and is not considered in this work.

Oxygen vacancies in STO alter the distribution of electron states in the lattice, as well as the physical lattice structure. In the presence of an oxygen vacancy, the distance between the two Ti atoms on either side of the vacancy increases. It is shown that the atomic radii of oxygen and different ionic states of Ti are as follows: O : 1.35 Å, Ti⁴⁺ : 0.605 Å, and Ti³⁺ : 0.67 Å [30]. In the presence of an oxygen vacancy, the Ti atoms reduce from the 4+ state to the 3+ state. For a unit cell, the lattice constant is equal to two radii of the Ti atom in the center, plus one radius from both of the O atoms on either side of Ti. We calculate the lattice constant, using these atomic radii values, for bulk STO,

$$a_{bulk} = 2 (O_{radius} + Ti_{radius}^{4+}) = 3.9165 \text{ Å}$$

 $a_{bulk} = 2 (1.35 + 0.605) = 3.9165 \text{ Å}$

close to the value for bulk STO, 3.905 Å. For an oxygen vacancy,

$$a_v = 2 (O_{radius} + Ti_{radius}^{3+}) = 4.04 \text{ Å}$$

 $a_v = 2 (1.35 + 0.67) = 4.04 \text{ Å}$

which comes out to be 0.1255 Å larger than the value calculated for bulk. This induces tensile strain around the oxygen vacancies. For 2.5% oxygen vacancies, the change in lattice constant from bulk would be $\Delta a = 0.0065$ Å.

Luo *et al.* show that an oxygen vacancy results in a shift of the charge density in the Ti 3d-eg state, as seen in figure 2.3 below, taken from [31]. The Ti atoms are pulled towards the oxygen vacancy, stabilizing a polarization in STO.



Figure 2.3: Electronic density of Ti³⁺ 3d state. Electronic density shifts as a result from an oxygen vacancy. Image taken from Luo *et al.* [31].

PL and CL studies have shown that oxygen vacancies have an activation energy $E_A = 0.24$ eV below the conduction band of STO [27], and that the Ov diffusion barrier is 0.6 – 0.98 eV, whereas the theoretical values for Sr and Ti are 3.3 - 4.9 eV and 2.8 - 4 eV respectively [27], suggesting that oxygen vacancies migrate through STO much more easily than Sr or Ti. This can result in ionic conduction via migration of oxygen vacancies, so it is important to distinguish between electronic and ionic conduction in transport analysis.

Bulk STO is an incipient ferroelectric – it has a suppressed ferroelectric phase, remaining paraelectric down to near 0K [32]. Under strain, however, ferroelectricity in STO has been measured experimentally [33]. Ferroelectricity in STO thin films is complicated,

exhibiting out of plane and in plane ferroelectric phases, and are dependent on the lattice parameters, which are effected by strain [34]. The strain-phase diagram for STO, constructed by thermodynamic analysis and phase-field simulations, shows that even just an order of 1% biaxial strain in STO will shift the T_c of STO to near room temperature [35]. It is shown through theoretical calculations that STO possesses spontaneous polarization in the out of plane or (001) direction under compressive strain, and in plane polarization under tensile strain [36]. From this, we suspect that our STO strained films on Si may be ferroelectric. This can be verified by piezoresponse force microscopy (PFM) but we do not currently have conclusive data on this.



Figure 2.4: Phase diagram of STO. Image taken from [37].

This phase diagram, Figure 2.4 above taken from [35], was calculated by Y. L. Li *et al.* [37] using Landau free energy calculations using spontaneous polarization $\mathbf{p} = (p1,p2,p3)$ and structural order parameters $\mathbf{q} = (q1,q2,q3)$ as order parameters.

In the transition from a cubic to tetragonal phase at 105K, the oxygen octahedron undergoes a rotation. This causes the out of plane lattice constant to expand while the in plane lattice constants continue to shrink, as temperature decreases [38]. Our thinner samples, however, are under strain due to Si and are not thick enough to relax. This strain complicates the structural transition.

Grain boundaries in STO are something to keep in mind, but are more prevalent in pulsed laser deposition (PLD) and sputtering methods than in MBE. Grain boundaries are also introduced through methods involving Ar^+ milling/irradiation to induce oxygen vacancies. This is because sputtering and Ar^+ milling are destructive to the sample and impart large amounts of energy which can allow atoms and molecules to break and reform bonds. Grown by MBE, our samples are shown to be single crystalline structures by x-ray diffraction, and oxygen vacancies are induced by control of O₂ pressure during growth, rather than by Ar^+ irradiation. For these reasons, grain boundaries should not play a large role in our analysis. Grain boundaries would show up in TEM images, where a shift in the crystal orientation would be seen.

III. GROWTH PROCEDURE

The STO/Si samples were grown by molecular beam epitaxy (MBE) in a system equipped with reflected high energy electron diffraction (RHEED), to monitor the growth quality and progress, combined with a quartz crystal monitor to estimate growth rates. 2 inch Si (100) boron doped (p-type) wafers were cleaned with a 2.5% solution of hydrofluoric acid, diluted with dionized water for 30 seconds to etch the Si oxide and passivate the surface with hydrogen to help prevent surface oxidation while transferring the sample. P-type wafers were chosen to distinguish the n-type STO from Si electronically. Additionally, some contaminants within the oxide layer are removed during the HF etch. The Si wafers were then treated with ozone O₃ for 20 minutes to clean off organic, carbon-based, compounds on the surface. The wafers were mounted on molybdenum sample holders and placed in the load lock. (Previous users had an issue with molybdenum diffusing into their samples when using oxygen plasma. The molybdenum holders used in this study were cleaned and baked at 600° C for one hour, and then baked again up to 1100° C (need accurate temperature) in the growth chamber.) The load lock was baked at 150° C for 1 hour before the samples were transferred into main buffer chamber, which stays at a base pressure on the order of 1×10^{-10} torr. The base pressure of the growth chamber was on the order of 1×10^{-10} torr with liquid nitrogen cooling.

The ozone treatment causes there to be a fairly uniform oxide on the surface. To remove this oxide layer from the Si, a "cleaning" procedure or recipe was used. This published recipe, performed in the growth chamber, introduces Sr with a substrate temperature (Ts) at 550° C (Sr flux rate). At this point the Sr bonds with the O molecules on the surface.

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The substrate temperature is then raised to 1100° C, giving the Sr-O molecules enough energy to leave the surface, leaving behind a clean Si 100 interface, verified by a 4x1 reconstruction RHEED image, as shown in figure 3.1. To begin growth of STO, Ts is lowered back down to 500° C and oxygen (O₂) is then introduced to a pressure of $\sim 1x10^{-7}$ torr. Sr and Ti are then introduced simultaneously to begin growth. Growth is stopped after 1.5-4 minutes to verify crystalline growth via RHEED, annealing to 700-800° C as necessary, and then growth is resumed. Sr and Ti cell temperatures were calibrated for stoichiometric STO growth at $\sim 600^{\circ}$ and $\sim 1600^{\circ}$ C respectively. During growth the temperatures are not usually modified, however stoichiometric growth is controlled by closing shutters to cells as needed. The thickness of STO films range from 4 nm to 60 nm thicknesses.





Before BFO and LAO growth, the STO/Si samples were taken out of the chamber to check the quality of the crystalline films and for electrical and magnetic measurements to establish a baseline. The STO/Si wafers were then cut into small squares, roughly 1cm by 1cm, and then mounted along with similarly sized pieces of an STO substrate on silicon

wafers with indium. Once loaded into the growth chamber, following the same loading process as above, STO was grown, as per above but without the cleaning recipe, for about 1 minute in order to get a Ti terminated surface by verified by RHEED (describe method of determining termination). BFO and LAO films, ranging in thickness, were then grown on the STO/Si and STO samples. The following two paragraphs detail the LAO and BFO growth procedures, respectively.

Rather than separate La, Al, and O sources, LAO thin films were grown using an electron beam deposition on an LAO target. This method is possible because La and Al have similar vapor pressures and sticking coefficients, unlike Sr and Ti. The current used for the electron beam was 44 mA (the current reading dropped to 35mA with the oxygen plasma on). Ts for LAO growth was 790° C. LAO was grown at varying thicknesses with an oxygen pressure of 1×10^{-7} torr.

BFO, like STO, was grown using sources of Bi and Fe, as well as oxygen plasma instead of molecular oxygen. O_2 was introduced to a pressure of 1×10^{-6} and then the plasma was started, with a final oxygen plasma pressure of 3×10^{-6} . Similar to the STO process, growth was modulated through closing shutters for short periods of time to preserve stoichiometry. An overpressure of bismuth is desired because iron reacts easily with oxygen forming iron oxides which would be detrimental to our samples, so the RHEED must be monitored closely for any signs of having too much Fe.

1x1 reconstructions of STO (010), (110), and (210) planes are shown in figure 3.2 below. The (110) plane reflections come from Sr atoms, whereas the (010) and (210) plane reflections come from Ti atoms. Examples of Sr rich STO and Ti rich STO are shown in figure 3.3. As can be seen, in (a) for example, in the (110) plane we start to see a 2x1 reconstruction when the stoichiometry gets off balance in favor or Sr.



Figure 3.2: RHEED patterns of STO. Reflection patterns show (a) STO (010) (b) STO (110), and (c) STO (210) planes.



Figure 3.3: RHEED patterns of Sr and Ti rich STO. 2x1 reconstruction RHEED reflection patterns show (a) Sr rich STO growth and (b) Ti rich STO growth.

IV. STRUCTURAL ANALYSIS

X-ray Diffraction

After growing the samples, XRD was performed to investigate the quality of the STO films with a Bede D1 four circle x-ray diffractometer using Cu k α x-rays and Si channel cut crystals. High angle 20- ω survey scans were taken to verify the crystalline structures grown and check for second phases. The high angle scans were also performed at various spots on the 2" wafers in order to map the surface and verify uniformity of the STO film on the Si wafer. ω -scan rocking curves were taken in high resolution alignment mode about the STO (002) peak to determine crystalline quality and observe any strain effects. ω -scans were also performed in this mode to calculate the lattice constant c along the [001] direction. Asymmetric scans were also performed around the (011) and (024) peaks to extrapolate the in-plane lattice constants and verify the orientation of STO on Si. Grazing angle x-ray reflectivity scans were performed to determine the thickness of the samples. XRD was performed on the STO/Si samples as well as the bulk Si wafers and the bulk STO substrates purchased from commercial vendors for comparison.

STO/Si vs. STO substrates

A comparative XRD study was done on STO/Si grown here by MBE and STO substrates purchased from vendors. Figure 4.8 below shows high angle survey scans of STO/Si and STO substrates. The STO (001), (002), and (003) peaks can be seen for all three samples. Figure 4.1 shows one of our samples of 9.6 nm STO grown on Si by MBE, an STO substrate from MTI, and an STO substrate from an unknown vendor. The full width half max values for the STO 002 peak are, respectively, 342.7, 50, and 36 arc seconds. The

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FWHM of thin films, such as the 9.6nm STO film shown here, are not indicative of film quality because of thin film broadening of the diffraction peak. The thin film broadening increases with decreasing film thickness. The FWHM of the 9.6nm STO film grown on STO is comparable to those seen by Eom *et al.* [26].



Figure 4.1: XRD Comparison of STO/Si by MBE and STO substrates. Comparison of 9.6nm STO/Si grown by MBE with STO substrates purchased from MTI and from an unknown vendor.

Survey Scans

Figure 4.2 below shows survey scans for a few samples at various STO thicknesses. The STO (001) and (002) peaks can be seen around $2\theta = 22.5^{\circ}$ and 46.2° respectively, as well as the Si (004) substrate peak at $2\theta = 69.09^{\circ}$. The bulk value for STO (002) is 46.5° . For thinner samples, the STO peaks shift slightly to the left, indicative of elongation in the [001] direction from compressive in-plane strain due to Poisson's ratio (the tendency for a material to expand in one direction when compressed in other directions). We sometimes see a peak at 33° which is a multiple diffraction peak from Si that looks like Si (002) [39]. This peak can be removed from the survey scan by rotation of several degrees in ϕ and would then reappear at the ϕ angles noted in reference [39]. During growth, sometimes a second phase of STO (011) starts to form in the [001] growth direction. We see this second phase STO (011) at $2\theta = 32.5^{\circ}$ and the samples that have this XRD peak are not used for further investigation.



Figure 4.2: XRD survey scans of STO. Wide angle survey scans of a few samples at 4.5nm, 8.6nm, and 29.5nm.

Second Phase

Figure 4.3 shows a survey scan of a sample with second phases. We see (011) STO at 2θ = 32.5° growing in the out of plane direction. Although interesting, we are not looking in to these samples; for now we are only investigating the single crystalline films. XRD data without peaks corresponding to second phases or other unidentified peaks was the first filter that determined whether we would investigate the sample further.



Figure 4.3: XRD survey scan of STO (011) second phase. (011) Second phases appear in the [001] growth direction.

Wafer Uniformity

Figure 4.4 shows XRD mapping for 59.6 nm STO/Si. A survey scan was taken at 5 different positions on the 2" wafer. Position 1 is at the center of the wafer, and position 5 is near the edge. All positions show peaks for STO and Si. The STO (001), STO (002), STO (003), Si (004) and Si (004) k β peaks appear at all 5 positions and have close to the same intensities and full width at half maximum (FWHM). Position 5 shows two extra peaks which are representative of anatase TiO₂ (112) and (224) planes, seen at 2 θ = 38.21° and 82.15° respectively. These planes are seen on TiO₂ grown on Si (001) by MOCVD [40], as well as TiO₂ on Si by hydrothermal epitaxy and chemical precipitation.

The d-spacing for these two peaks is very close to the d-spacing for the theoretical values of the (112) and (224) planes at 38.57° and 82.67° respectively. The formation of TiO_2 may be due to lack of Sr near the edges. We conclude that there are no large differences in the crystalline structure across the 2" wafer growth area except very near the edge (up to ~2mm from the edge) where TiO_2 appears.



Figure 4.4: XRD mapping of 2" STO/Si wafer. Several survey scans mapping positions on a single 2 inch wafer of 59.6nm STO/Si. Position 1 is at the center of the 2 inch wafer, with each position moving closer to the edge. Position 5 is near edge of the wafer and shows some TiO2 second phases. These scans are scaled linearly on the x and y-axes.

<u>FWHM – Crystalline Quality</u>

Rocking curves of a 29.5nm STO film on Si is shown below in figure 4.5. Rocking curves are taken by changing, or "rocking", the incident angle of the x-rays, ω , to the sample while holding the detector angle, 20, fixed. These scans are done in high resolution alignment, using two Si (220) channel-cut crystals to monochromate the x-rays. The FWHM from rocking curves is used to gauge crystalline quality – the sharper the peak, the higher the quality of the crystal. The peaks on the side are diffraction fringes due to constructive interference with the film. These are similar to what are seen in the XRR scans, discussed later. The θ values from these scans were used to determine the out



Figure 4.5: Rocking curve of STO (002). A rocking curve is shown of 29.5nm STO/Si about the STO (002) peak.

Asymmetric Scans

Asymmetric scans were taken about the theoretical value of STO (011), $2\theta = 32.3964^{\circ}$, to examine the STO (011) plane. Since the (011) plane is roughly 45° from the [001] growth direction, the sample must be tilted 45° with respect to the incident beam in order to see reflections from the (011) plane. This was done by tilting the sample back, rotating X chi by 45°, while setting $2\theta - \omega$ to 32° . At this point there will be four phi values, 90° apart, where the (011) plane will be in line to satisfy the Bragg condition. Using the exact 2θ value at which the (011) peak is seen, the d-spacing for this plane can be calculated and used along with the d-spacing in the (001) direction, which correlates to the lattice parameter 'c', to gain insight to the other two lattice parameters, 'b' and 'a'. Figure 4.6 below shows an asymmetric scan for the STO (011) plane.



Figure 4.6: Asymmetric scan of STO (011). Peak found at 2theta = 32 degrees.

The lattice constants can be calculated through Bragg's law:

 $2dsin(\theta) = n\lambda$



Figure 4.7: Schematic of Bragg's law. Diffraction of X-rays off a crystal lattice with lattice spacing d is shown.
Or:

$$d = \frac{n\lambda}{2\sin(\theta)}$$

Where d is the distance between the atomic layers, λ is the wavelength of the x-ray, and theta is the angle of the incident x-rays to the surface. In the [001] growth direction, d equates directly to the lattice constant c. When looking at the (011) plane, d gives us the length of a line bisecting a triangle created by c, a, and the (011) plane.



Figure 4.8: Schematic of lattice parameters. Constants relative to the d-spacing of the STO (011) plane are shown.

The low FWHM for the STO (002) peaks show that quality crystalline STO films have been grown at varying thickness. The reproducibility of the XRD data for all samples shows that successful MBE growth of good quality STO films has been achieved up to 80nm. For all the samples studied and presented here, all XRD peaks have been identified and no second phases occur. The ability to see additional STO peaks from off axis/asymmetric scans gives some insight to the in-plane strain effects due to Si.

001 Lattice Parameter vs Sample Thickness

The survey scans for multiple samples, ranging in thickness, were shifted so that the Si (004) peak lined up with what was measured for the Si substrate. The d-spacing was then calculated for each sample using the 2θ value for the STO (002) peak, giving the lattice parameter 'c' for each sample. The lattice parameter is shown as a function of thickness in figure 4.9. As can be seen, the thickest sample shown, 60nm, has a lattice constant very close to the accepted bulk value, a = c = 3.905 Å. As the samples decrease in thickness, STO is strained due to the Si lattice. The STO 002 peak shifts, relating to an increase in the lattice parameter 'c'. The data agrees with the critical thickness of 11.5 nm calculated in the introduction. Above 11.5 nm, the lattice relaxes and c decreases to its bulk value. The in plane data had a significant amount of error and we were unable to obtain a conclusive data set. The 20.3 nm STO/Si sample, circled in red on the figure, was grown at 650° C, which is different than the rest of the samples shown which were grown Ts = $700 - 720^{\circ}$ C. The 8.6 nm STO/Si circled in blue showed bad RHEED during growth, and another 8.6 nm STO/Si sample was grown immediately after under the same growth conditions. These samples were kept in order to see the effect of different growth conditions on the transport properties of the films.



Figure 4.9: Out-of-plane lattice parameter as a function of film thickness. Plot of the out of plane lattice parameter c calculated from XRD STO (002) peak centers and the in plane lattice parameter a from the STO (024) peaks as a function of thickness are shown. The data point in the red circle is 20.3nm STO/Si grown at Ts = 650° C, and the data point circled in blue is 8.6nm STO/Si which showed bad RHEED during growth.

XRD was also performed on samples of similar thickness, 8.7 to 9.6 nm, but for different growth conditions, such as oxygen pressure and substrate temperature shown in figure 4.10 (a) and (b) below. Both of these variables show a trend in the lattice constant. It is important to keep in mind though that there is some slight variation in thickness, which is shown to effect the lattice constant.



Figure 4.10: Out of plane lattice parameter c as a function of oxygen pressure and temperature. Out of plane lattice constant plotted as a function of (a) oxygen pressure during growth and (b) substrate temperature during growth for STO films, all near the same thickness.



Figure 4.10, continued: Out of plane lattice parameter c as a function of oxygen pressure and temperature. Out of plane lattice constant plotted as a function of (a) oxygen pressure during growth and (b) substrate temperature during growth for STO films, all near the same thickness.

X-Ray Reflectivity

X-ray reflectivity (XRR) scans were used to determine the thickness of the samples. A couple scans, for (a) 60nm and (b) 4.5nm STO on Si respectively, are shown below in figure 4.11. The reflection fringes, due to constructive and destructive interference, can be seen. The model fits the thickness and density of the material, as shown in the figure.



Figure 4.11: XRR scans of STO films. X-ray reflectivity scans are shown for (a) 59.6nm STO/Si and (b) 4.6nm STO/Si.

Atomic Force Microscopy and Scanning Electron Microscopy

Atomic Force Microscopy (AFM) was performed on all STO/Si samples to study surface quality and roughness. Using AFM we can see if the surfaces are smooth and clean, or if they have holes or second phases. These holes and second phases on the surface can also be seen using a Scanning Electron Microscope (SEM). Figure 4.12 shows AFM images and corresponding SEM images of a few samples.



Figure 4.12: AFM and SEM images of STO. (a) and (b) AFM and SEM image respectively from 4.6nm STO/Si. (c) and (d) AFM and SEM image respectively from 59.6nm STO/Si.

Many samples were grown, and not all of them successfully. Figure 4.13 below shows AFM and SEM images of a sample with second phases. Both show structures on the surface oriented perpendicular to each other. In the SEM image the crystallites appear very structured and uniform. This second phase is the STO (011) that is seen in XRD. These are examples of samples that were NOT used for transport measurements in this study.



Figure 4.13: AFM and SEM images of STO (011) second phases. (a) and (b) AFM and SEM image respectively showing a sample containing second phases, perpendicular STO (011) crystallites on the sample surface. These correspond to the STO (011) peak seen in fig. 4.3 XRD survey scan at 2theta = 32.5°.

Transmission Electron Microscopy

TEM was performed by Jesus Cantu and Arturo Ponce-Pedrazu at the University of Texas, San Antonio, shown in figure 4.14 below. The TEM confirms clean interfaces with no formation of amorphous SiO_x at the interface of STO/Si. The dark line at the interface could be a change in the charge, but it does not look indicative of an amorphous region. STO and Si are crystalline up to the interface, and the selected area diffraction patterns (SADP) show a smooth, crystalline transition across the interface.

Selected area electron diffraction (SAED) patterns



Figure 4.14: TEM of STO/Si. TEM and SADP for 59.6nm STO on Si was performed by Jesus Cantu and Arturo Ponce-Pedraza at the University of Texas, San Antonio.

Ellipsometry

Ellipsometry was performed on the STO/Si samples with an M-2000 Spectroscopic Ellipsometer from J. A. Woollam Co., Inc. The ellipsometer is equipped with an FLS-300 light source, containing a 75W Xe arc lamp, and has a spectral range of 210nm - 1000nm(or 1eV - 6eV). The data was analyzed with Complete EASE software provided by the same company.

Incident light is linearly polarized at a 45° angle and reflects off the sample surface at discrete angles. The light is consisted of s and p polarized light, which are the parallel and

perpendicular components. Upon reflection, the amplitude and phase of the s and p polarized light shift and are measured by the detector. The instrument measures the parameters Ψ and Δ , the angle and phase difference, of polarized light reflected from the sample, governed by the following relation:

$$\rho = \tan(\psi) e^{i\Delta}$$

Where ρ is the reflectance ratio, tan(Ψ) is amplitude ratio upon reflection, and Δ is the phase shift.

Spectra were taken at 55, 65, and 75 degrees from the normal to the surface of the sample. The model used to fit the spectra consisted of a STO/Si heterostructure, using Cauchy relation parameters from Herzinger *et al.* [41] for Si, and a general cauchy layer for the STO where we could either fit or specify the Cauchy parameters. The software fit A, B, and C from the Cauchy relation:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$

Where $n(\lambda)$ is the energy dependent index of refraction. A spectrum for one sample is shown below in Fig. 4.15. The following table lists the values fit for A, B, and C, as well as the thickness calculated for each sample. The thicknesses were estimated by growth rates from RHEED during growth. We compare the data to thicknesses calculated from XRR, shown in the table at the end of the chapter.



Variable Angle Spectroscopic Ellipsometric (VASE) Data

Figure 4.15: Ellipsometry scans of STO films. Ellipsometry data for sample STO(60nm)/Si. The black dotted lines show the fit to the data.

One can also calculate n and k, the real and imaginary components of the index of refraction, at a specific wavelength from psi and delta, and a model can be fit to the data to get a continuous function of n and k. The imaginary component of the index of refraction, k, corresponds to absorption which can be plotted as a function of energy (wavelength). Absorption will be very low or zero for low energy values, where the photons do not have enough energy to excite electrons across the band gap, and will jump up once the energy of the photons is equal to or greater than the band gap energy. Theoretically, there will be a linear region of the graph which will intercept the energy axis at the band gap if k^2 or $k^{1/2}$ is plotted for direct and indirect band gaps respectively [42].

The model uses Lorentz oscillators to fit the data. Lorentz oscillators are dipole oscillations due to a force linear with position (Hook's law force). To first order, an electron in a semiconductor near the band gap acts like a Lorentz oscillator.

This technique was used for our samples to find the band gap as a function of thickness and oxygen pressure during growth. Figure 4.16 below shows the direct band gap for our samples as a function of thickness, as well as a function of oxygen pressure during growth. A trend can be seen of a lower band gap with higher thickness and higher oxygen pressure.

Not much time was spent in analysis regarding this technique due to anisotropy in the dielectric constant of STO resulting from strain. However, the effects of strain on the STO band gap are calculated theoretically by Berger *et al.* [43].

Table 4.1 below summarizes the structural analysis data for each sample.

	Th (XRR)	Th (Ell)	Rate				FWHM
Sample	(nm)	(nm)	(Å/m)	O2 (torr)	Tsub (°C)	RMS (nm)	(arcseconds)
S1	4.60		0.58	4.00E-08	700	0.122	259
S2	4.50		0.56	4.00E-08	700		190
S3	5.40		0.47	4.00E-08	700	0.182	
S4	8.21		0.55	4.00E-08	700	0.242	331.6
S5	8.60		0.41	4.00E-08	700	0.229	179.3
S6	8.57		0.39	4.00E-08	700	0.201	186.5
S7	9.57	11.00	0.37	4.00E-08	700	0.185	342.7
S8	14.75	16.00	0.49	4.00E-08	720		
S9	20.30	20.00	0.68	4.00E-08	650	0.152	
S10	29.50		0.35	4.00E-08	700	0.19	
S11	59.60	61.00	0.46	4.00E-08	720	0.444	
S12	9.70	10.90	0.42	2.00E-07	700	0.173	
S13	8.85	10.20	0.35	4.00E-07	700		
S14	13.60		0.45	4.00E-07	700		
S15	9.50	9.60	0.37	8.00E-08	700	0.177	
S16	8.90		0.34	4.00E-08	500		
S17	9.30		0.36	4.00E-08	600		

Table 4.1: Structural data of each sample from XRD, Ellipsometry, and AFM as well as relevant growth conditions.



Figure 4.16: Band gap energy vs. thickness and oxygen pressure. Calculated direct band gap of STO as a function of (a) thickness and (b) O₂ pressure during growth.

V. TRANSPORT ANALYSIS

Contacts

Electrical measurements were performed in a Quantum Design Physical Property Measurements System (PPMS). Current-voltage (IV) curves, resistivity, and Hall measurements were taken at various temperatures in a Van der Pauw configuration on rectangular pieces of STO/Si.

Contacts to each one of the samples were fabricated by W deposition using the gas deposition function of our FEI NanoLab Helios 400 scanning electron microscope (SEM). First, 200x200 um areas were milled, using Ga ions, at a depth of 3-10nm into the STO film, depending on the thickness - enough to probe the thin film but not far enough to reach the interface. Immediately after milling, W was deposited into the milled areas to form 200x200 um W contact pads. The reason for milling and depositing W was to: a) get through any possible surface layer, b) achieve ohmic contact (W on Si creates Ohmic contact and W was available in the SEM GIS) c) increase the W and In contact adhesion, since In on STO was not sticking as well, and d) to reduce the contact resistance (it has been shown that Ar ion milling reduces the resistivity of STO [12]). Four W contacts were deposited using the Gas Injection System that were 200x200 um in dimension, one on each corner of a square sample. The samples were wired to the PPMS sample pucks with Au wire pressed into the W contact pads using In to ensure connection. Most groups use a wire bonder with Al wires to make contact [44], and we plan to use this method in the future but at the time did not have the parts required.

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Method

Van der Pauw measurements utilize these four contacts pads in order to measure an average resistivity value, as well as to measure Hall voltages. Current is sent through the sample into one contact and out another, denoted by I+ and I- in the diagram below, while the voltage is measured across the remaining two contacts, denoted by V+ and V-. The four leads are switched, electronically, in order to send current across all four sides, as well as across the two diagonals, of the sample. Current is sent both ways (positive and negative current) in all six of these configurations, giving a total of twelve measurements. The measurements across the diagonals of the sample are used in calculating the Hall effect, to determine the carrier concentration, whereas the measurements along the side of the sample, which we call "off diagonal" configurations, are used in calculating the resistivity. Together, these two sets of data can be used to calculate the mobility as shown by Van der Pauw. Measurements were taken from 300K down to 3K and between +/- 9T.



Figure 5.1: Schematic of the 4 Van der Pauw contacts on a square sample.

Evolution of Electrical Measurement Set-Up

Originally the electrical measurements were taken using the bridge electronics of the PPMS system itself. We saw some reproducible results, but the data were very "noisy" at low temperatures and measurements were not completed in certain cases. The sensitivity of the PPMS electronics was such that the measurements were least noisy when measuring voltages on the order of 1-10 millivolts, and with the resistances values (MOhms) of our samples at low temperatures, the PPMS electronics could not source a current low enough (1-100 nA) to achieve that 1-10 millivolt range. Below 1uA the current from the PPMS electronics was not very stable. We monitored the output current of the PPMS electronics with an oscilloscope and decided it was too noisy for our measurements.

We decided to use a current source (Keithley 6221) and an electrometer (Keithley 619), and wired these to the leads connected directly to the sample in the PPMS, bypassing the bridge electronics of the PPMS system. We started out by taking measurements manually; setting the current output on the current source and recording by hand the voltage readings on the electrometer. We took some IV curves at various temperatures and attempted to perform a Hall effect measurement. The IV's were linear, and the resistances were consistent with the resistances we were measuring with the PPMS electronics, but the electrometer was not sensitive enough to see the changes of resistance (a few Ohms) produced by the Hall effect. Nothing was automated in this set up, the measurements were taken manually and were tedious, but taking the measurements

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manually and reading instruments I could control directly gave me a much better feel for what was going on and what I was looking at.

We then tried taking measurements with just a Keithley 2400 source measurement unit (SMU) that can source current and measure voltage simultaneously, and the Keithley 7065 Hall card (used to switch the I and V configuration on the leads electronically). This set up allowed use to source current potentially from 1mA down to 1pA, though I usually took measurements between 1uA and 100uA, while also giving a greater range of voltage sensing, 10uV to 200V, than the PPMS electronics. This set up worked better our STO/Si samples but the data was still "noisy". Again, the measurements came out consistent with what we were measuring with all the other setups.

Finally, we switched to a Keithley 6221 current source meter and a Keithley 2182A nanovoltmeter together with the 7065 Hall card. This set-up yielded the most flexibility in current and voltage ranges, and gave us the least "noisy" measurements. The current source has a current range of 100fA to 100mA with an output resistance of more than 10¹⁴ Ohms, and the nanovoltmeter can measure 1uV up to 10V with an input resistance of more than 10⁹ Ohms. The Hall Card has an input impedance of more than 10⁹ Ohms and 10¹⁴ Ohms, in low and high resistance modes respectively. This setup allowed reliable measurements up to 1 GOhm. We considered using a lock-in amplifier but this only had an input resistance of 10⁶ Ohm, which was on the order of the resistance of the samples we were measuring, and it also sourced voltage instead of current. Converting the lock-in amplifier to a current source is possible by adding a resistor in series that is much larger

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than the resistance we are measuring, but since the resistance of our samples changes by several orders of magnitude with temperature, it was not practical. The Keithley 6221 current source, 2182 nanovoltmeter, and 7065 Hall Card were integrated with the PPMS temperature and magnetic field control through Labview, enabling us to automate IV curves as well as Hall measurements at many fields and at different temperatures.

Current-Voltage Characteristics

Before electrical measurements were made, appropriate current ranges were determined after taking current-voltage (IV) measurements at several temperatures to verify ohmic contacts, i.e. linear IVs. Transport and magnetotransport measurements were only taken at the current ranges where the IV curves were linear. Since the sample resistance changes by several orders of magnitude from 300K down to 3K, different current ranges were needed for different temperatures. IV curves were taken every 50K from 300K down to 50K, and at 25K, 12K, and 3K as well to ensure ohmic contacts. The currents used ranged from 1nA to 10uA. Figure 5.2 below shows some examples of IV curves at different temperatures. All twelve Van der Pauw configurations were tested every time.



Figure 5.2: IV measurements for STO/Si at various temperatures. Shown for 60nm STO sample, the different colored lines represent the 12 different configurations measured on the sample in the Van der Pauw configuration.

Resistivity vs. Temperature

Resistance as a function of temperature was measured for each sample. Figure 5.3 below shows the resistance and resistivity curve of each sample. The resistance at room temperature is very close to the resistance measured for the Si substrates. As the temperature decreases, the resistance increases. Between 50K and 200K, the resistance seems to settle to an almost constant value. The thinner samples, 3-8.5nm, approach 1MOhm around 200K, whereas the thicker samples, 15-60nm, fall in the 1k-100kOhm range. The resistance of all the samples begins to increase again at low temperatures. The samples below 8.6nm (except for 8.2nm) all follow pretty close to the same R vs. T curve, while the thicker samples show much different resistance values at temperatures below 250K. This may be evident of some critical thickness at which the resistance behavior changes for the STO films, where the resistance is not thickness dependent until it reaches a critical thickness where some structural or electronic reconfiguration occurs, similar to that of the critical thickness, in LAO films, of the formation of a 2DEG at the interface of LAO and STO discussed in the introduction. The resistivity thickness dependence and the carrier concentrations (~1x10²⁰ cm⁻³) were motivation to further investigate transport. Figure 5.4 shows the resistivity as a function of thickness at 200K.

An important factor here is the number of oxygen vacancies in the STO film, which is controlled by the oxygen pressure during growth. The data for the three 8nm samples varies significantly and does not seem to fit in consistently with the rest of the data. We believe that the differences in the data result from different oxygen vacancy densities, despite the fact that they were grown at roughly the same oxygen pressure. The oxygen valve in the chamber is sensitive and occasionally, if careful attention isn't paid, the oxygen pressure can increase by an order of magnitude. The data for all other thicknesses are more consistent.



Figure 5.3: Resistivity vs. temperature for all samples. (a) Linear and (b) log scale resistivity vs. temperature.



Figure 5.4: Resistivity as a function of thickness at 200K.

Hall Effect

Hall effect measurements, shown in figure 5.5 below, were also performed on each sample. The resistance is measured as a function of magnetic field, and from this the resistance at zero field is subtracted, to get delta Rd.

$$R_H = \frac{d}{B} \Delta R_{diagonal} \longrightarrow \Delta R_{diagonal} = \frac{R_H}{d} B$$

Where R_H is the Hall resistance, d is the thickness, B is the applied magnetic field, and $\Delta R_{diagonal}$ is the resistance measured across the diagonal of the sample minus the resistance measured at B = 0. The slope of the graph, $\frac{R_H}{d}$, gives the type of carriers seen, positive for p-type carriers and negative for n-type carriers [45]. At 300K we see a positive Hall effect denoting that we have p-type carriers. As we cool down, by 200K we see a negative Hall effects, indicative of n-type carriers. Between 300K and 200K the carriers transition from p-type to n-type. As the temperature drops down below ~50K, the Hall effect starts competing with the magnetoresistance effect, resulting in different slopes for positive and negative magnetic fields. In the case of the thinner samples, the Hall effect is still positive at 300K but becomes very noisy below 250K, indicating that there are not many carriers (electrons) for these temperatures in STO.



Figure 5.5: Hall Effect of STO/Si. Hall Effect for 59.6nm STO/Si at (a) 300K, (b) 200K, and (c) 3K showing p-type carriers at 300K and n-type carriers at lower temperatures is shown. The Hall Effect competing with MR can be seen in (c).



Figure 5.5, continued: Hall Effect of STO/Si. Hall Effect for 59.6nm STO/Si at (a) 300K, (b) 200K, and (c) 3K showing p-type carriers at 300K and n-type carriers at lower temperatures is shown. The Hall Effect competing with MR can be seen in (c).

From the R vs. T data combined with the Hall measurements, it looks like we primarily see p-type carriers near room temperature, and as the samples are cooled down n-type carriers start to dominate. We believe these n-type carriers are coming from the STO film, however it is unclear whether this is a bulk STO effect, or an effect coming from the STO/Si interface or the surface of STO. One way we can gain insight into this is by looking at the resistivity to see if there is any thickness dependence.

Magnetoresistance

Standard quadratic magnetoresistance (MR) curves are seen clearly at 300K. MR is negative or flat between 200K and 50K. As we approach lower temperatures, near 3K, negative MR curves, in the shape of an "M", are seen, where it is positive at low fields and starts to turn negative at high fields. The negative MR is indicative of the Kondo effect [46] but can also be due to several other effects such as electron localization or magnetic second phases. This behavior is typical for most of our films.

The Kondo effect is related to an upturn in the resistance at low temperatures. Two groups, Li *et al.* [47] and Lee *et al.* [48] see an increase in resistance at low temperatures in electrolyte gated STO and attribute this to the Kondo effect. Lee *et al.* also see a negative MR effect for in-plane-MR measurements.



Figure 5.6: Magnetoresistance (MR) of STO/Si. Graphs for 14.8nm STO/Si at (a) 3K, (b) 12K, (c) 100K, (d) 200K, and (e) 300K are shown.



Figure 5.6, continued: Magnetoresistance (MR) of STO/Si. Graphs for 14.8nm STO/Si at (a) 3K, (b) 12K, (c) 100K, (d) 200K, and (e) 300K are shown.



Figure 5.6, continued: Magnetoresistance (MR) of STO/Si. Graphs for 14.8nm STO/Si at (a) 3K, (b) 12K, (c) 100K, (d) 200K, and (e) 300K are shown.

At 300K, we see a Hall effect with a positive slope, which corresponds to p-type carriers, and we also see positive MR which is typical of orbital scattering of carriers. At first glance, one might attribute the p-type carriers to Si, but the resistivity we measure at 300K is lower than the resistivity of our Si wafers, 1-5 Ohm cm. At 200K, we see negative Hall effect, corresponding to n-type carriers. At lower temperatures, however, the Hall effect becomes very small and non-linear because it competes with a much larger MR effect. As can be seen, the Hall effect is on the order of a few Ohms, while the MR in these samples is a greater effect. For this reason, it is difficult to fit the Hall data, and our calculations of the sheet carrier concentration (n_s) , volume carrier concentration (n_v) , and mobility (μ) are estimates at best. We can still, however, get an idea of the orders of magnitude of these values in our samples.

Figure 5.7 below shows the conductivity (σ), carrier concentration (n_s), volume carrier concentration (n_v), and mobility (μ), calculated following the Van der Pauw method[45], as a function of thickness at 200K, and table 5.1 below that shows the transport values for each sample at 200K, 100K, 50K, and 3K. Since we measure p-type carriers at 300K, the values calculated included the thickness of the Si substrate. This is why the values are different than for the rest of the temperatures.



Figure 5.7: Transport calculations for each sample. (a) conductivity, (b) carrier concentration, (c) volume carrier concentration, and (d) mobility as a function of thickness at 200K for STO are shown.



Figure 5.7, continued: Transport calculations for each sample. (a) conductivity, (b) carrier concentration, (c) volume carrier concentration, and (d) mobility as a function of thickness at 200K for STO are shown.

Thickness	Resistivity	Hall Resistance	Conductivity	pv	ps	Mobility
nm	Ohm cm	cm ³ /C	(Ohm cm) ⁻¹	cm⁻³	cm ⁻²	cm²/V s
4.5						
4.6	3.73559	886.07689	0.2677	7.04E+15	2.11E+14	237.19888
5.4	3.78154	1001.90145	0.26444	6.23E+15	1.87E+14	264.94553
8.2	9.16892	992.13889	0.10906	6.29E+15	1.89E+14	108.20678
8.6	5.13761	958.06571	0.19464	6.52E+15	1.95E+14	186.4808
8.6	6.0626	884.45208	0.16495	7.06E+15	2.12E+14	145.88654
9.6	4.28273	993.86852	0.2335	6.28E+15	1.88E+14	232.06402
14.8	9.65369	867.12149	0.10359	7.20E+15	2.16E+14	89.82285
20.3	13.63782	1716.60998	0.07333	3.64E+15	1.09E+14	125.87133
29.5	21.02884	682.38456	0.04755	9.15E+15	2.74E+14	32.44993
59.6	6.46557	1918.84649	0.15467	3.25E+15	9.76E+13	296.779

Table 5.1: Values for each sample calculated from transport measurements. Data shown at (a) 300K,(b) 200K, (c) 100K, (d) 50K, and (e) 3K.

Table 5.1, continued: Values for each sample calculated from transport measurements. Data shown at (a) 300K, (b) 200K, (c) 100K, (d) 50K, and (e) 3K.

Thickness	Resistivity	Hall Resistance	Conductivity	n _v	n _s	Mobility
nm	Ohm cm	cm ³ /C	(Ohm cm)⁻¹	cm⁻³	cm⁻²	cm²/V s
4.5	0.54048					
4.6	0.45264					
5.4	0.47991	-0.5076	2.08375	1.23E+19	6.64E+12	1.05771
8.2	0.05147	-0.02479	19.42733	2.52E+20	2.06E+14	0.48169
8.6	0.52611	-0.98513	1.90074	6.34E+18	5.45E+12	1.87247
8.6	0.51004	-1.87309	1.96063	3.33E+18	2.87E+12	3.67244
9.6	0.13517	-0.08512	7.3983	7.33E+19	7.04E+13	0.62971
14.8	0.06856	-0.05524	14.58558	1.13E+20	1.67E+14	0.80569
20.3	0.02409	-0.06476	41.51009	9.64E+19	1.96E+14	2.68821
29.5	0.1084					
59.6	0.0488	-0.08117	20.4932	7.69E+19	4.58E+14	1.6634

Thickness	Resistivity	Hall Resistance	Conductivity	n _v	n _s	Mobility
nm	Ohm cm	cm ³ /C	(Ohm cm)⁻¹	cm⁻³	cm⁻²	cm²/V s
4.5	2.39767					
4.6	2.24421	-0.94185	0.44559	6.63E+18	3.05E+12	0.41968
5.4	2.52214	-1.25847	0.39649	4.96E+18	2.68E+12	0.49897
8.2	0.08065	-0.03871	12.39996	1.61E+20	1.32E+14	0.47997
8.6	10.16615	-5.62655	0.09837	1.11E+18	9.54E+11	0.55346
8.6	4.58869	-2.42305	0.21793	2.58E+18	2.22E+12	0.52805
9.6	0.56065	-0.5376	1.78364	1.16E+19	1.11E+13	0.95888
14.8	0.23776	-0.04	4.20597	1.56E+20	2.31E+14	0.16824
20.3	0.02127	-0.08	47.02211	7.80E+19	1.58E+14	3.76171
29.5	0.45825	-0.10212	2.18222	6.11E+19	1.80E+14	0.22284
59.6	0.05191	-0.11138	19.26431	5.60E+19	3.34E+14	2.1456

Table 5.1, continued	: Values for each sar	mple calculated	from transport measurements	. Data shown
at (a) 300K, (b) 200H	K, (c) 100K, (d) 50K,	and (e) 3K.		

Table 5.1, continued: Values for each sample calculated from transport measurements. Data shown at (a) 300K, (b) 200K, (c) 100K, (d) 50K, and (e) 3K.

Thickness	Resistivity	Hall Resistance	Conductivity	n _v	n _s	Mobility
nm	Ohm cm	cm ³ /C	(Ohm cm) ⁻¹	cm⁻³	cm⁻²	cm²/V s
4.5	21.13384					
4.6	17.77394					
5.4	19.31875	-12.22479	0.05176	5.11E+17	2.76E+11	0.63279
8.2	0.14371					
8.6	122.69939	-36.22363	0.00815	1.72E+17	1.48E+11	0.29522
8.6	38.8405	-3.96589	0.02575	1.57E+18	1.35E+12	0.10211
9.6	2.19107					
14.8	0.88929					
20.3	0.02399	-0.09742	41.67549	6.41E+19	1.30E+14	4.06
29.5	1.68775					
59.6	0.06385	-0.13297	15.66114	4.69E+19	2.80E+14	2.08247

Thickness	Resistivity	Hall Resistance	Conductivity	n _v	n _s	Mobility
nm	Ohm cm	cm ³ /C	(Ohm cm) ⁻¹	cm⁻³	cm⁻²	cm²/V s
4.5						
4.6						
5.4	0.10672	-9.40E-03	1.13E-06	6.64E+12	1.06E+00	
8.2	20.63817	-309.76812	0.04845	2.02E+16	1.65E+10	15.00948
8.6						
8.6						
9.6						
14.8	41.77777	-227.08454	0.02394	2.75E+16	4.07E+10	5.43554
20.3	0.03452	-0.03864	28.97169	1.62E+20	3.28E+14	1.11957
29.5	0.02624	264.81294	-9748.73373	0.00378	6.40E+14	1.89E+09
59.6	0.15969	-0.30323	6.26198	2.06E+19	1.23E+14	1.89885

Table 5.1, continued: Values for each sample calculated from transport measurements. Data shown at (a) 300K, (b) 200K, (c) 100K, (d) 50K, and (e) 3K.

Comparison to Literature

STO has undergone many transport studies, whether it be bulk STO doped with Nb or irradiated with Ar milling to induce n-type carriers, STO gated with electrolytes, or STO thin films with induced oxygen vacancies on various substrates.

Yamada *et al.* [49] performed PL on four types of STO: undoped STO, Nb doped STO, La doped STO, and Ar+ irradiated STO. The undoped STO was annealed under oxygen flow for 24 hours. All samples were 0.5 mm thick. They measure PL as a function of carrier density with different doping levels, and see a redshift in the PL with increasing carrier density for all dopants. They also see a blue shift and broadening in the PL peaks with increasing temperature. Yamada *et al.* estimate carrier densities of $1.78 \times 10^{22} * x$, where *x* is the fraction of Nb replacing Ti in STO, and measure a band gap of 3.246 eV.

Bruno *et al.* [50] study Ar+ irradiated STO. They see very linear Hall and MR curves, and an RvT curve that gradually decreases quadratically with temperature, much different than the curves we see. They calculate sheet mobilities and carrier concentrations of $\mu = 1699 \text{ cm}^2/\text{Vs}$ and $n = 2.45 \times 10^{17} \text{ cm}^{-2}$ at 5K. Ar milling to induce n-type carriers is very destructive to the sample, and creates many defects and grain boundaries, which will certainly effect electrical properties of the sample.

Parkin *et al.* [47] performed transport measurements on electrolyte gated STO structures. They see two regimes, metallic samples for high gate levels, and samples with a diverging resistance at low temperatures, similar to what we see, for low gate levels. They calculate carrier densities on the order of $\sim 2 - 4x10^{13}$ cm⁻² for their metallic samples, close to what we calculate in our samples, however our samples are not metallic. Parkin *et al.* use a 2D VRH model that fits their data well for temperatures below 50K.

 $SrTiO_{2.5}$ thin films were grown by PLD by Parez-Casero *et al.* [51]. This is a much higher level of oxygen vacancies than we have in our samples. Parez-Casero *et al.* measure resistance increasing with decreasing temperature, like our films, but at a much more gradual rate, almost a linear or quadratic relationship. They fit their data to a 3D VRH model between 60K and 200K. They also see a dependence of the resistivity on growth temperature, with their samples grown at 700° C exhibiting metallic behavior.

Liu *et al.* [52] grew oxygen deficient STO films on LAO substrates by PLD. To introduce oxygen vacancies, they annealed their samples at high temperatures in a low oxygen pressure environment. They see metallic behavior down to a MIT at 78K, where the resistance increases six orders of magnitude as the temperature decreases to 10K. They see the carrier concentration, $\sim 1 \times 10^{19}$ cm⁻³, drop an order of magnitude between 300K

and 10K. They also measure bulk STO single crystal, annealed under the same conditions as the films, to be metallic over the whole temperature range.

Different groups have measured very different results for the electrical properties of STO, but there are a number of factors that differ among the groups and play important roles. Bulk STO vs. thin film STO, the growth method of STO thin films – MBE, PLD, the method of introduction of defects and dopants – growth conditions, annealing, milling, and the substrate choice of STO thin films, LAO being a commonly used substrate. In our case, STO is grown on Si, in which the doping type and concentration in Si is important.

Transport in 20nm STO films with oxygen deficiencies, grown on LAO substrates by laser MBE, has been measured by Cai *et al.* [53]. Their results are shown below in figure 5.8 (a). Their high oxygen pressure samples behave like semiconductors, with increasing resistivity at low temperatures, and their low oxygen pressure samples have metallic behavior, with resistivity decreasing at low temperatures. It should be noted that oxygen pressures during their growth only vary by one order of magnitude, $5x10^{-6}$ to $5x10^{-5}$ mbar, and result in resistivity that vary by almost five orders of magnitude at 50K. This means the resistivity of STO is very sensitive to oxygen pressures during growth, and we have to be very careful during our growth to keep the oxygen pressure constant. Although our study is mainly on thickness dependence, whereas Cai *et al.* only had one thickness, our samples resemble their higher oxygen pressure samples.


Figure 5.8: Comparison of resistivity vs. temperature for STO films. (a) Graph of resistivity vs. temperature for samples grown at different oxygen pressures taken from Cai *et al.* [41]. (b) Resistivity as a function of temperature for 20.3nm STO/Si for comparison.

In a recent paper on conduction in Ca-doped BiFeO₃ films, by Yang *et al.* [54], oxygen vacancies are said to naturally occur and "act as donor impurities to compensate for calcium acceptors and maintain a highly stable Fe³⁺ valence state" in these Ca-doped BFO films. Using the Nernst-Einstein relation, shown below, they estimate the ionic conductivity in order to determine if the conduction in their films is electronic or ionic in nature.

$$\sigma_{ion} = \frac{n_{Vo}e^2D}{k_BT}$$

Where σ_{ion} is the ionic conductivity, n_{Vo} is the oxygen vacancy density, and *D* is the diffusivity of the oxygen vacancies. Yang *et al.*, based on Fick's Second law, assumed an inter-diffusion length for one week was on the order of their film thickness, about 100nm, estimated the diffusivity of oxygen vacancies to be ~10⁻¹⁷ cm² s⁻¹. We figured a similar D for our samples, due to the fact we have a similar perovskite material and we see similar

behavior in polarizing the films and observing the stability of polarization with time (not presented in the thesis), and estimate an oxygen vacancy density of $\sim 10^{19}$ cm⁻³. To arrive at this, we looked at the difference in the carrier concentration of our samples ($\sim 10^{19}$ cm⁻³) and the intrinsic carrier concentration in bulk STO films ($\sim 10^5$ cm⁻³, much less than 10^9 cm⁻³ for Si, which has a smaller band gap of 1.1eV vs. 3.2eV for STO), which is negligible compared to the carrier concentration of our films. Since each oxygen vacancy produces two electron carriers to the lattice, the oxygen vacancy density is roughly on the same order as the carrier concentration of our films. With these values, we estimate the ionic conductivity of our samples to be 1.4E-6 Ohm⁻¹ cm⁻¹. This is much less than the conductivity we measure, so we can safely say that our conduction is electronic rather than ionic in nature.

Discussion

At this point a few questions are still unanswered: why we see thickness dependence in the resistivity, what the origin of the p-type and n-type carriers we see is, and why we see the trend in MR as a function of temperature. In an attempt to answer these questions, we turn back to basic physics and consider what we have. The Si wafers that we used were ptype, Boron doped Si(001) with ρ =(1-5) Ω cm and n-type, Phosphorus doped Si (001) with ρ =(1-5) Ω cm. According to literature [55], shown below in figure 5.9 (a), the expected doping concentration is 3×10¹⁵ atoms/cm³ to 1×10¹⁶ atoms/cm³ and mobility 450 cm²/V s to 430 cm²/V s at T=300K for the p-type and 1×10¹⁵ atoms/cm³ to 4×10¹⁵ atoms/cm³ and mobility 1362 cm²/V s to 1283 cm²/V s at T=300K for the n-type. The 3" n-type (p-type) wafer were 375 μ m thick and at room temperature, an estimated R=27 – 133 Ω . This expected because of the impurity doping. The resistance is expected to decrease from T=300K to T=50K-100K by less than 10% where it has a minimum and then starts rapidly increasing because of the freeze-out of the carriers (holes for the p-type), and the carrier density is less than the impurity concentration. This is shown in figure 5.9 (b), also taken from [55].



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Figure 5.9: Carrier density vs. temperature, and resistivity vs. impurity doping for Si. (a) Carrier density in Si as a function of temperature, showing the behavior difference in intrinsic and extrinsic carriers. (b) Resistivity in Si and GaAs as a function of doping concentration. Both images are taken from S. M. Sze and M. K Lee, Semiconductor Devices – Physics and Technology [55].

The resistance of the Si wafers is measured, but around 250K the resistance dramatically increases to the measurement limit of our system, 1 GOhm. What we measure here is the contact resistance, not the actual resistance of Si. The resistance of Si is not expected to change much as a function of temperature until the carriers freeze out at around 50K [56].

SrTiO₃ thin films were deposited by MBE (Molecular Beam Epitaxy) on Si with Oxygen partial pressure of $P_{O_2}=4\times10^{-8}$ Torr to $P_{O_2}=4\times10^{-7}$ Torr so that they were Oxygen deficient intentionally and hence were n-type.

Using the bulk lattice constant of STO, the volume of a unit cell of STO $V_{u.c.}$ is calculated.

$$V_{u,c} = (3.905 \times 10^{-8} cm)^3 = 5.955 \times 10^{-23} cm^3$$

From this, the number of unit cells $N_{u.c.}$ in a cm³ is:

$$N_{u.c.} = \frac{1 \ cm^3}{5.955 x 10^{-23} \ cm^3} = 1.679 x 10^{22}$$

Since there are three oxygen atoms (six halves) per unit cell, this results in 5.038×10^{22} Oxygen atoms per cm³.

$$3 * N_{u.c.} = 3 * 1.679 \times 10^{22} = 5.038 \times 10^{22}$$

Given that the number of oxygen vacancies we have is on the order of 1×10^{20} cm⁻³ (on the same order as the carrier concentrations measured, where each oxygen vacancy contributes two electron carriers), I calculate that there is a 0.2% oxygen deficiency (δ) in our STO films on Si. This is consistent with the variation of lattice constant that we get from XRD as a function of Oxygen pressure.

$$\delta = \frac{1x10^{20}}{5.038x10^{22}} * 100 = 0.2\%$$

The expected resistivity of oxygen deficient STO is about $5 \times 10^3 \ \Omega \text{ cm} [57]$ and $5 \times 10^2 \ \Omega \text{ cm} [58]$ at T=300K and varies by a factor of 2 with temperature [57] so the resistance of our films must be at least $1 \times 10^7 \ \Omega$ for the thicker films much larger than the resistance of the Si wafer. We measured $\sim 10^2 \Omega$ (RT, p-type substrate). The resistance of the Si wafer is in parallel to the resistance of the STO thin films. We cannot use a simple parallel-resistor model though unless we know that we have an Ohmic contact. The resistance of the junction between Si and STO has to be considered especially in the case of the p-Si/n-STO junction.

For the n-STO/n-Si junction, the band diagram is more "leveled", the Fermi level of Si and STO are aligned with a small conduction band offset. So, we believe that the STO/n-type resistance is the resistance of the Si substrate. The resistance as a function of temperature for STO/ n-Si is shown below in figure 5.10.



Figure 5.10: Resistance as a function of temperature for STO on p-type and n-type Si substrates. 9.6nm and 8.7nm STO on p-type and n-type Si respectively are shown.

In the case of p-Si/n-STO, we believe there is a formation of a space charge region, similar to a p-n junction, at the interface, where holes are diffusing into STO and electrons into Si. Following the derivations outlined in [55] for p-n heterojunctions, we calculate the built in bias V_{bi} of the space charge region at the interface.

$$V_{bi} = k_B T \ln(\frac{N_A}{N_D})$$

$$V_{bi} = 25 \ mV \ ln(\frac{7x10^{15}}{1x10^{20}})$$

$$V_{bi} \approx 239.2 \, mV$$

Where k_BT is the Boltzmann constant times temperature, which at room temperature is about 25 meV, N_A is the carrier density of Si, and N_D is the carrier density of STO.

Since the space charge per area in each region must be equal,

$$x_p N_A = x_n N_D$$

and $N_D \gg N_A$, then $x_p \gg x_n$, where x_n and x_p are the lengths of the depletion region in the n-type and p-type materials respectively. In other words, the depletion width is almost all in Si. The data suggests that the thin STO layers do not have enough carriers to "screen" the effect at the interface, and have a higher resistance. As thickness increases, and once the space charge region is fully screened, the STO films have more carriers to contribute, and lower resistances are measured.

Variable Range Hopping – Thermionic Emission

In the temperature range between 250K and 300K, the resistivity scales with thickness and p-type carriers are measured. We know that we are not directly measuring Si because the resistivity we measure, 10⁻² Ohm cm, is much less than expected for our Si wafers, 1-5 Ohm cm. We fit the data to a variable range hopping (VRH) model to get an idea of the conduction mechanism. VRH models conduction of systems that are disordered and have localized charge-carrier states [59]. The VRH equation is as follows:

$$\rho = \rho_o \exp\left[\left(\frac{T_o}{T}\right)^n\right]$$

$$\ln(\rho) = \ln(\rho_o) + \left(\frac{T_o}{T}\right)^n$$

We plot $\ln(\rho)$ as a function of $\frac{10,000}{T}$ and fit the curve using:

$$y = a + bx^c$$

Where in our case, $y = \ln(\rho)$, x = 1/T, and we fix b = 1 because T_o is already accounted for. This leaves two fitting parameters, $a = \ln(\rho_o)$ and c = n, the exponent. Figure 5.11 below shows a curve for 4.6 nm and 59.6 nm and table 5.2 below has the fit data for all samples. $T_o = 10,000$ K correlates to about 1 eV.



Figure 5.11: VRH models for STO/Si. (a) 4.6 nm and (b) 59.6 nm STO/Si, holding To = 10,000K and fitting the exponent are shown.

Thickness	Temperature Range		ln(ρ _o)			
(nm)	(K)	Т _о (К)	(Ohm cm)		n	
4.6	240 - 290	10000	-44.70	±0.73	1.0072	±0.0052
5.4	240 - 270	10000	-50.44	±0.76	1.0358	±0.0047
8.2	260 - 300	10000	-36.42	±0.87	0.9538	±0.008
8.6	255 - 285	10000	-43.18	±0.12	1.0010	±0.0009
8.6	250 - 275	10000	-40.84	±0.21	0.9845	±0.0016
9.6	260 - 290	10000	-46.10	±0.4	1.0228	±0.0028
14.8	270 - 300	10000	-38.99	±0.29	0.9828	±0.0025
20.3	270 - 300	10000	-33.20	±0.46	0.9281	±0.0048
29.5	280 - 300	10000	-35.26	±0.35	0.9618	±0.0033
59.6	260 - 280	10000	-38.20	±0.27	0.9678	±0.0023

Table 5.2: Values for VRH fit of STO/Si for all thicknesses.

Since the exponent for all thicknesses are ~1 ($\ln R \sim T^{-1}$), rather than VRH what we appear to have is thermionic emission of holes that have been injected from Si to STO. These holes have to jump over the STO barrier from the Si conduction band to our metallic contacts, so we see band bending of STO toward the metal contact. T₀ here represents the energy to jump over this barrier. Another way for the fitting here would be to fit R₀ and T₀ instead of n. This would give us an activation energy for the holes to jump over the barrier. Normally, at this temperature, we do not expect the hole concentration in Si to change so what we are seeing is that the holes that reach the metallic contact over STO are thermally activated and at the transition where the slope of resistivity as a function of temperature clearly changes, around 250K, we measure a transition from p-type to n-type so at that point p=n. As temperature decreases, the resistance goes up because there are fewer holes that have been thermally excited.

I fit two samples, 4.6 nm and 59.6 nm STO/Si, to the same model but held the exponent fixed to n = 1, and kept $ln(\rho_0)$ and T_0 as fitting parameters, shown below in figure 5.12, with the data in table 5.3. For these two samples, the model gave T_0 as 103475K and

8614K for 4.6 nm and 59.6 nm STO/Si respectively. From To, the energy barrier E_b can be calculated using the following relation,

$$To = \frac{E_b}{k_B}$$

where k_B is the Boltzmann constant. E_b for each sample is also shown in table 5.3. The values are consistent with studies of band bending at the surface of STO [20]. The energy barrier is higher for the thinner films than the thicker films.



Figure 5.12: VRH model fitting the activation energy. T_o, the activation energy, for (a) 4.6 nm and (b) 59.6 nm STO/Si is shown.

Thickness	Temperature		$\ln(\rho_o)$		
(nm)	Range (K)	n	(Ohm cm)	$T_{o}(K)$	E _b (eV)
4.6	240 - 290	1	-45.01 ±0.93	10347.5 ±240	0.891644 ±0.021
5.4	240 - 270	1	-52.05944 ± 1.00	11816 ±255	1.018185 ± 0.022
8.2	260 - 300	1	-35.03371 ±1.09	8085.8 ±303	0.696753 ± 0.026
8.6	255 - 285	1	-43.21822 ±0.15	10044.1 ±41	0.8655 ± 0.004
8.6	250 - 275	1	-40.27821 ±0.26	9304.6 ±68	0.801777 ± 0.006
9.6	260 - 290	1	-47.00003 ±0.52	11100.5 ±143	0.95653 ± 0.012
14.8	270 - 300	1	-38.42585 ± 0.37	9244 ±104	0.796555 ± 0.009
20.3	270 - 300	1	-31.24087 ±0.55	7182.9 ±157	0.61895 ± 0.014
29.5	280 - 300	1	-34.10646 ± 0.44	8400.7 ±128	0.723888 ±0.011
59.6	260 - 280	1	-37.14 ±0.34	8614.5 ±90	0.742311 ±0.008

Table 5.3: Values for the VRH model, holding n = 1 and fitting To and $ln(\rho o)$.

Upon closer evaluation of the above fits, the values given for ρ_o is on the order of 10^{-19} ; this does not make sense physically – this is not the right fit for the data. The fits above are insensitive to T_o and to the exponent, n. The resistivity, ρ_o , is the only "sensitive" parameter to the fits and varies from 10^{-52} to 10^{-31} with temperature as well as with thickness. The data must be normalized with respect to this thickness dependence in order to properly model the temperature dependence. We normalize the resistivity for each sample, $(\rho_o - \rho)/\rho_o$, where ρ_o is the resistivity at the highest temperature used in the above fits, and plot this as a function of thickness, as shown below in figure 5.13.



Figure 5.13: Normalized resistivity as a function of thickness for STO/Si films.

We fit this plot to an exponential function,

$$y = y_o + A_1 e^{\frac{-x}{t_1}}$$

fixing y_0 to 10.5 and t_1 to 1 and letting A_1 vary to get a more physical fit. This resulted in an A_1 value of 11892.61. Using this, we multiply the resistivity of each sample by the exponential factor,

$$y_o + A_1 e^{\frac{-d}{t_1}}$$

We use the fitting parameters $y_o = 10.5$, $A_1 = 11892.61$, $t_1 = 1$, and d is the thickness of the sample, to eliminate the thickness dependence of the resistivity. A plot of this normalized resistivity as a function of temperature is shown below in figure 5.14 for each sample. The legend denotes the thickness of each sample in nm.



Figure 5.14: Resistivity as a function of temperature after removing thickness dependence. (a) Linear scale and (b) log scale after resistivity is multiplied by the exponential factor to eliminate the thickness dependence. The legend denotes the thickness of each sample in nm.



Figure 5.14, continued: Resistivity as a function of temperature after removing thickness dependence. (a) Linear scale and (b) log scale after resistivity is multiplied by the exponential factor to eliminate the thickness dependence. The legend denotes the thickness of each sample in nm.

The thickness dependence is taken out from the temperature dependence of the resistivity and from Fig. 5.14, we can see that the temperature dependence of the resistivity overlaps for the thinner films. There are still a few issues to consider: In this temperature range (250K-300K), the type of carriers we measure by the Hall Effect is changing from p-type carriers to n-type carriers. There is also a change in the number of electrons and not only holes as the thickness decreases and as the temperature decreases. Finally, the Electric Field due to the intrinsic bias has not been taken into account. For an estimated built-in bias of 0.5V, and for d=10 nm, $E=5\times10^7$ V/cm which is significant. Also, as mentioned, the resistivity varies exponentially as a function of thickness and temperature. All of these factors must be taken into consideration, and it is difficult to decouple them all and normalize the resistivity. As can be seen in (b) of figure 5.14, the slope of each curve is about the same but the offset vary over three orders of magnitude. We are still in the process of finding the right fit of the data to explain the conduction mechanisms.

Magnetoresistance Characteristics

Near the "critical point", $T_c \sim 250$ K, where the transition happens for rapid resistance increase to slower resistance increase, the Hall effect is very weak if any and there is a transition from p-type carriers above T_c to n-type well below T_c . More importantly for the localization argument, there is no MR around T_c and the MR is positive above T_c and negative further below T_c (T< T_c). Also, the MR remains negative down to low temperatures but becomes slightly positive for samples that have resistances close to Si substrate resistance (the "orange line") on Fig. 1. The downturn from positive to negative MR, at high B, occurs only for samples that their resistance is below the "orange line" (STO/ n-Si) and near the T when they cross the "orange line", as seen in figure 5.15 below. The negative MR may be attributed to the detrapping of localized carriers [60].



Figure 5.15: Resistance vs. temperature for all thicknesses, including the n-type substrate.

VI. CONCLUSIONS

STO thin films were grown on p-type Si substrates by MBE. The thickness of the films and oxygen pressure during growth were varied to study the effects of film thickness and oxygen content in the STO/Si structure. XRD and AFM verified good quality crystalline STO films with smooth surfaces. Transport measurements were performed to analyze the electrical characteristics of the STO films on Si, and an attempt to explain the resulting conductivity was made. The STO films are n-type doped due to oxygen vacancies at lower temperatures where p-type conductivity is measured at room temperature. STO/Si has been studied before but the thickness dependence we measure has not been seen. We believe the thickness dependence is related to the band bending and the interactions of ptype and n-type carriers at the interface, resulting in the formation of a space charge region. The data suggests a critical thickness must be reached to fully screen the space charge region, which results in lower resistivity for thicker samples. We also find that the carriers in STO are not mobile and may be localized as we get negative MR.

Our plan going forward is to make contact to the STO film and to the Si substrate and perform current-voltage measurements to characterize the heterojunction at the interface. Also, more transport and MR measurements need to be performed around the temperature, ~250K, where we see transition from p-type to n-type to characterize the change in carrier concentration. We will also finish the transport measurements on the samples with different oxygen pressures. In addition, we will try using a Hall Bar configuration as opposed to the Van der Pauw configuration in order to get better transport measurements. PFM measurements are currently being performed but are

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unfinished. These may help explain the ferroelectric property that may exist in the strained STO films.

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