Partial carrier freeze-out at the LaAlO3/SrTiO3 oxide interface

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Abstract
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Keywords
laalo3/srtio3, partial, oxide, carrier, interface, freeze-out

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ABSTRACT
High quality robust two-dimensional electron gas (2DEG) LaAlO$_3$/SrTiO$_3$ (LAO/STO) interfaces are produced using pulsed laser deposition and an acid-free substrate Ti-termination process, resulting in single unit cell terraces. Temperature dependent resistance measurements show two hysteresis anomalies around 80 K and 160 K. By using Hall measurements, we find an Arrhenius dependence in charge carrier density describing a partial carrier freeze-out below $\sim$80 K. We show that these two resistance anomalies are unrelated to the temperature dependence of the charge carrier density despite the tempting coincidence of the low temperature hysteresis feature and the freeze-out process. A two-carrier model is required to accurately estimate the activation energy of the thermally activated type charge carriers, which are found to be $\sim$5 to 7 meV. These results support the theory that oxygen vacancy defects contribute to the metallic conductivity at the 2DEG LAO/STO interface even for annealed samples.

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Despite intensive research, the two-dimensional electron gas (2DEG) interfacial conductivity between insulating perovskite oxides SrTiO$_3$ (STO) and LaAlO$_3$ (LAO) is still not completely understood. There is no universally agreed upon theory able to account for diverse properties of 2DEG. Some of these properties include semiconductorlike field-effect control of conductivity, tunable superconductivity, and ferromagnetism. These properties are not always observed together, which hints that this diversity may result from the interplay between various factors. An electron redistribution about the interface resulting from the polar discontinuity between the two materials and oxygen vacancy doping are two commonly discussed mechanisms.

The observed properties of this interface have evolved substantially since the initial discovery. It is now known that depositing at very low oxygen partial pressures results in a significantly increased carrier density and conductivity. This is due to the formation of oxygen vacancies throughout the STO bulk with the conductivity no longer confined to the interface. Higher deposition pressures ($\sim$10$^{-4}$ mbar) are now commonly used to remove this unwanted bulk conductivity. Furthermore, it has also become common to anneal samples in an even higher oxygen atmosphere ($\sim$10$^2$ mbar), while cooling from the deposition temperature in an attempt to further reduce the effect of oxygen vacancies. Perovskite materials are sensitive to defects. Variations from the ideal cubic perovskite structure can lead to pronounced macroscopic effects. Indeed, the STO structural phase transition that occurs around 105 K in the bulk also shows a significant impact on the electrical transport properties at the LAO/STO interface.

In this work, we report that an acid-free substrate titanium termination procedure results in conductive LAO/STO interfaces. We also show that the reduction in charge carrier density below $\sim$80 K is unlikely to be related to structural effects in contrast to a tempting misinterpretation nor to the resistance-temperature hysteresis anomalies observed at this interface at $\sim$80 K and $\sim$160 K. It is rather the result of a partial freeze-out of thermally ionized charge carriers.
The high quality LAO thin films used in this work were grown using our pulsed laser deposition (PLD) technique.\textsuperscript{17,18} The Ti-termination of commercially available 5 × 5 mm single crystal STO (001) substrates was achieved using the acid-free method.\textsuperscript{19,20} This method uses annealing at 1000°C in air and de-ionized (DI) water leaching to produce an atomically smooth Ti-terminated surface without the use of hazardous and highly toxic hydrofluoric (HF) acid. To ensure any SrO islands that form during the annealing stages were completely removed, hot (\(\sim 50^\circ\text{C}\)) DI water was used.\textsuperscript{21}

Two families of LAO/STO heterostructures were grown to ensure the generality of our results independent of the manufacturing approach: one—excimer—using a KrF excimer laser (248 nm) and the other—Solid State (SS)—using the second harmonic of a Nd:YAG solid state laser (532 nm). Each family consisted of multiple samples. The epitaxial LAO films were grown under \(10^{-4}\) mbar pressure of \(\text{O}_2\) with STO substrates held at 800°C during the deposition process. The laser repetition rate of 2 Hz and the fluence of approximately 1.5 J/cm\(^2\) were used. All films were annealed in 267 mbar \(\text{O}_2\) pressure, while cooling from the deposition temperature. Au/Pd contacts were deposited at room temperature in a Van der Pauw configuration also using PLD. Transport measurements were carried out in a Quantum Design Physical Property Measurement System. The temperature dependence of resistance was measured for several samples upon cooling and subsequent warming at a rate of 3.5 K/min within the range of 2 K–300 K with the applied current of 10 μA and 100 μA. The Hall measurements were performed over the field range of ±2 T using both field sweeping for each temperature and continuous temperature sweep mode at a set field. X-ray diffraction (XRD) and reflectometry (XRR) were measured using a PANalytical X’pert PRO X-ray reflectometer. XRR data were fitted using MOTOFIT,\textsuperscript{22} while the XRD fringes were fitted using the 1D interference function,\textsuperscript{23}

\[
I(Q) \propto \frac{\sin(\frac{1}{2}NmQa)^2}{\sin(\frac{1}{2}Qa)},
\]

where \(m\) is the diffraction order, \(a\) is the lattice parameter, \(Q\) is the momentum transfer, and \(N\) is the number of unit cells contributing to the interference. For thin epitaxial films, \(N\) provides a crystalline thickness of the film in unit cells.

Figure 1 shows typical Atomic Force Microscopy (AFM), XRD, and XRR results for our samples. Figure 1(a) confirms the Ti-termination procedure and LAO deposition resulted in an atomically smooth LAO surface with regular unit cell sized terracing. The XRD result in Fig. 1(b) shows that both lasers produced high quality crystalline growth of the LAO film as indicated by the resolved double LAO/STO peaks denoted in Fig. 1(d). A typical fit to the XRR Kiessig fringes and to XRD Laue fringes is shown in Figs. 1(c) and 1(d), respectively. A slightly reduced out of plane LAO lattice parameter of 3.76 Å was used to fit all samples. It differs from the bulk LAO parameter\textsuperscript{24} at 300 K by 0.03 Å. Out of plane compression is likely due to the in-plane tension of the STO lattice at the interface. The thickness estimates from both XRD and XRR measurements agree to within ±1 Å (Table I),

\[\text{FIG. 1.} \text{ (a) A typical AFM image of a } 3 \times 3 \mu\text{m}^2 \text{ surface of a LAO/STO sample shows regular unit cell sized terracing. (b) XRD for both excimer and Solid State (SS) samples showing the (001), (002), (003) STO and LAO diffraction peaks. Tiny peaks at 38.2°, 41.8°, 65.2°, 82.1° are unrelated to the 2DEG structure. (c) XRR results (black) and fit (red) of a SS sample. (d) XRD Laue fit (red) of the (001) peak of the same SS sample.}\]
TABLE I. Film thickness obtained from x-ray measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>XRD thickness (nm)</th>
<th>XRR thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid state</td>
<td>10.52</td>
<td>10.60</td>
</tr>
<tr>
<td>Excimer</td>
<td>9.02</td>
<td>8.93</td>
</tr>
</tbody>
</table>

indicating that the LAO films are epitaxially grown through their entire thickness. The film thicknesses were 10.5 nm (28 u.c.) and 9 nm (24 u.c.) for the SS and Excimer samples deposited for 120 s and 90 s, respectively. These results ensure that electron transport is characterized in a high quality crystalline LAO/STO interface.

The resistance and Hall measurements of samples from both families were carried out between 2 K and 300 K. Their $R(T)$ properties and carrier densities are typical of LAO/STO samples grown at high oxygen pressures ($>10^{-5}$ mbar) and/or annealed in oxygen.\textsuperscript{16–18} Our samples exhibit a sheet carrier density of $(2–7) \times 10^{15}$ cm$^{-2}$ and a sheet resistance of the order of $10^3$ Ω/□ at 2 K. Hall measurements exhibited a typical linear dependence on magnetic field at all temperatures up to $|B| = 2$ T.\textsuperscript{25} This behavior independently confirms that conductive LAO/STO samples can reliably be produced using the acid-free termination method proposed by Connell et al.\textsuperscript{19} The properties of so-produced samples are consistent with those produced from buffered hydrofluoric (HF) acid etched substrates.\textsuperscript{14,15} This method removes the requirement of using highly toxic HF acid. It requires only a furnace and de-ionized water, which is very accessible and viable for potential commercialization.

The inset in Fig. 2(a) shows a typical $R(T)$ dependence for our samples. Both the warming and cooling curves appeared almost identical. However, if a normalized resistance difference

$$\Delta R(T) = \frac{R_{\text{warming}}(T) - R_{\text{cooling}}(T)}{R_{\text{cooling}}(T)} \quad (2)$$

is plotted, two clear slightly irreversible features peaking at ~80 K and ~160 K are observed [Fig. 2(a)]. At these features, the resistance measured while warming is up to ~5% higher than that measured upon cooling. Similar results have been reported previously.\textsuperscript{7,12–15,25} In addition, we observed that the increased resistance measured during the warming cycle is time dependent,\textsuperscript{25} as also observed elsewhere.\textsuperscript{7,14,15} If held at constant temperature, the resistance measured during warming at these features reduces toward the cooling value over a period of approximately 1 h, indicating that the transition between high resistance and low resistance occurs gradually. These resistance features were suggested to be due to the formation of striped tetragonal STO surface domains.\textsuperscript{12,13}

Figure 2 shows that the onsets of the reduction in carrier density and the resistance difference anomaly appear to coincide at ~80 K. These coinciding features in $n(T)$ and $\Delta R(T)$ are tempting to associate one with another. Indeed, it was suggested that the reduction in carrier density might indicate the impact of a structural transition.\textsuperscript{25} Below, we show that these two effects, the reduction in carrier density and the irreversible resistivity at 80 K, are rather independent.

First, it is worth noting that upon field sweep measurements of carrier density, each value was measured during approximately 15 min [Fig. 2(b)], likely representing the equilibrium state of the system at any given temperature. However, the carrier density obtained by continuous sweeping temperature at a set field can include transient effects just like for the interface resistance measured in the same fashion, in particular, on warming due to slow kinetics of the domain formation.\textsuperscript{12} Both the transient and equilibrium measurements of the carrier density have shown no difference between cooling and warming within the experimental error, unlike the resistance in Fig. 2(a). This strongly suggests that carrier density freeze out is unrelated to the resistance irreversibility at 80 K. The data scattering above ~100 K is due to different field sweep directions for each of the two neighboring points and imperfect contact geometry of Hall measurements.

Second, an Arrhenius dependence with a small activation energy is expected for thermally ionized carriers from a shallow donor band close to the conduction band edge. The $n(T)$ behavior

![FIG. 2. (a) The normalized sheet resistance difference between the cooling and warming curves of a typical excimer and SS samples measured at 3.5 K/min. The inset shows the resistance cooling curve for the same excimer sample (the warming curve is indistinguishable). (b) Sheet carrier density as obtained by typical Hall measurements. The large symbols are for field sweep measurements in thermal equilibrium. The small symbol data are obtained by continuous temperature sweeps at ±2 T. The dashed lines are the corresponding Arrhenius fits.](https://www.scitation.org/doi/abs/10.1063/1.5112804)
[Fig. 2(b)] was found to be well described by an Arrhenius dependence \((n_0 \propto \exp[-E_a/(k_B T)])\) as shown by the dashed lines. The data exhibit no notable variations from the expected Arrhenius fit around 80 K and 160 K (Fig. 3). At the same time, the \(\Delta R\) curve shows a sharp decrease just above 80 K and 160 K [Fig. 2(a)]. If either of these sharp decreases were related to the reduction in carrier density, we would expect to see corresponding notable deviations from the expected Arrhenius dependence. Thus, thermal ionizations (and corresponding charge carrier density) alone does not support the irreversibility observed in \(\Delta R(T)\) [Fig. 2(a)] within the experimental error.

It is worthwhile adding the following: (i) the thermally activated ionization time scale is far shorter than any structural changes. (ii) The density variations due to any possible temperature lagging of the temperature sweep in our experiments with 3.5 K/min sweep rate would be too small to produce a notable difference in the charge carrier density. (iii) An imbalance of thermally activated processes influenced by a temperature lag caused by sweeping temperature up and down would have produced a uniform hysteresis over the entire measured temperature range; in contrast, the hysteresis is dramatically peaking at \(\sim 80\) K and \(\sim 160\) K. (iv) The LAO layer is only a few nanometers thick with the STO substrate being only 0.5 mm thick, making any substantial temperature gradient within the sample unlikely.

Based on the above experiments and their analysis, we believe the feature observed in \(\Delta R\) at \(\sim 80\) K is independent of the change in the charge carrier density around this temperature. The increased resistance with increasing temperature can be explained without requiring a change to the carrier density. It can instead be caused by the increased electron scattering upon the filamentlike (twin) domain formation below 105 K as a result of cubic to tetragonal structural transition of the crystal lattice so that the conductivity becomes inhomogeneous due to the need for the carriers to cross domain boundaries possessing higher resistivity.\(^{12,13,26}\)

A similar explanation and arguments should also be valid for the 160 K feature, which also occurs without notable changes to the density of charge carriers compared to the Arrhenius fit. Indeed, it was found that STO single crystals experience structural phase transitions near a surface with similar randomly oriented tetragonal domains at a temperature, which is \(\sim 45\) K higher than the analogous 105 K structural transition occurring in the bulk of STO crystals.\(^{27,28}\)

A more detailed analysis of the carrier density provides further insight into the nature of the interfacial conductivity in the LAO/STO heterostructure as follows. Two models have been used to fit the Hall carrier density between 30 and 140 K: one is an entirely thermally activated (Arrhenius) model

\[
n(T) = n_0 e^{E_a/k_B T}
\]

and the other is a two-carrier model with an additional temperature independent term \(n_1\), which represents the metallic conductivity of the LAO/STO interface establishing a nonzero carrier density at lowest temperatures,

\[
n(T) = n_1 + n_2 e^{E_a/k_B T}.
\]

Both samples have approximately the same minimum carrier density at 20 K [Fig. 2(b)]. Upon fitting Eq. (4) to the data, we used \(n_1 = 2.3 \times 10^{13}\) cm\(^{-2}\) for the minimum carrier density, while \(n_2\) and \(E_a\) were two free fitting parameters. Similarly, for the single-carrier model [Eq. (3)], the free variables were \(n_0\) and \(E_a\).

In Fig. 3, both models are shown to describe data obtained for the charge carrier density rather accurately: the solid lines are the single-carrier model fits and the dashed lines correspond to the two-carrier model fits for both excimer and solid state LAO/STO 2DEG heterostructures. The data plotted by the open symbols are obtained by subtracting \(n_1\) from the total density \(n(T)\). These data sets have steeper slopes, i.e., larger activation energies. Figure 2(b) shows the corresponding two-carrier model fits in a semilogarithmic scale. The fitting parameters for both models are given in Table II. The temperature independent carriers support metallic conductivity assumed for the LAO/STO interface, while supplementary thermally excited carriers likely caused by oxygen vacancies also contribute to the conductivity. For both samples, the activation energy is increased by 4 meV upon using the two-carrier model compared to the single-carrier model. The minimum observed at \(\sim 20\) K in Fig. 2(b) can be associated with the Kondo-like upturn\(^{29}\) measured in \(R(T)\) at the same temperature [the inset of Fig. 2(a)].

The \(E_a\) values obtained agree with those published for the LAO/STO interface,\(^{30,31}\) as well as with those for similar multilayered LAO/STO structures,\(^{32}\) for LaSrAlTaO\(_3\)/STO interfaces with higher electron mobilities,\(^{33}\) and for the amorphous CaHfO\(_3\)/STO interface despite having no polar discontinuity.\(^{34}\) The discrepancy obtained for optical measurements of carrier density below 100 K in Refs. 16 and 36 can be explained by photo-excitation of a shallow donor band.

![FIG. 3. Charge carrier densities measured between 30 and 140 K for typical excimer and SS samples with closed symbols showing the raw data from Fig. 2(b), while open symbols are after the subtraction of \(n_1 = 2.3 \times 10^{13}\) cm\(^{-2}\) [Eq. (4)]. The solid and dashed lines are fits of Eqs. (4) and (3), respectively.](image)

**TABLE II.** Fitting parameters used in Fig. 3. Uncertainties were calculated from the linear fitting error.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Single carrier</th>
<th>Two carriers</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>(n_0 \times 10^{13}) cm(^{-2})</td>
<td>(E_a) (meV)</td>
</tr>
<tr>
<td>Solid state</td>
<td>5.1</td>
<td>1.6 ± 0.1</td>
</tr>
<tr>
<td>Excimer</td>
<td>7.9</td>
<td>2.8 ± 0.2</td>
</tr>
</tbody>
</table>
The differences in $E_a$ obtained between the models show that whilst not changing in magnitude the donors may be energetically deeper from the conduction band than those suggested in reports using an entirely thermally ionized model.\textsuperscript{20,31} Note that remarkable agreement for $E_a$ within the two-carrier model is obtained with nonlinear high-field Hall results.\textsuperscript{2,24}

All these systems have the common factor of using PLD with STO substrates. It is therefore possible that the donor sites are a potentially unwanted by-product of the highly energetic PLD process, similar to how STO surfaces are known to become conductive after being bombarded with high energy ions during ion beam etching.\textsuperscript{17,24} This assertion is supported by the possibility to control the activation energy and high temperature carrier concentration for the amorphous CaHfO$_3$/STO interface by varying the laser fluence.\textsuperscript{18}

In summary, as an independent proof, we have fabricated Ti-terminated STO substrates by the technologically friendlier process of annealing and DI water leaching to robustly produce atomically smooth single unit cell high terraced surfaces, used to create conductive LAO/STO interfaces. We have also shown that the two irreversible resistance anomalies are unrelated to the observed freeze-out process coinciding well with the feature measured at $\sim$80 K, and do not correspond to any changes in carrier density regardless of being in thermal equilibrium or in a thermally dynamic nonstabilized state. However, the observation of these features may depend on the level of the total charge carrier concentration and mobility. If the resistance is too high, no features are observed. If the resistance drops over many orders of magnitude, the small features are too small to distinguish. This is supported by the need of narrow bridges for the observation of these hysteresis features in Ref. 13: a high total charge carrier concentration might result in high conductivities masking these hysteresis effects. The charge carrier freeze-out can be accurately described using a partially thermally ionized model indicating the presence of both free and localizable carriers, i.e., metallic-like and thermally activated type.

See the supplementary material for more information on Hall measurement data.

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