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Hall bar Measurements
Properties of Reduced Graphene Oxide and Au-Si-doped GaAs

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1 Abstract in English and Danish

English

We have measured sheet and contact resistance in thermally reduced graphene oxide (rGO) thin films. The measurements were made using a Hall bar geometry which has not been done before with rGO. The sheet resistance was found to be 120 kΩ which is much higher than that of graphene. Contact resistance was found to be negligible compared to sheet resistance at room temperature. By resistance curve derivative analysis (RCDA) on a small amount of data it was found that the dominant transport mechanism in rGO is Efros-Shklovskii Variable Range Hopping (VRH) with some contribution from Mott VRH.

Due to difficulties in measuring Hall voltage arising from the conduction mechanism in rGO mobility and carrier density were not determined.

Conductance in rGO as a function of annealing time and temperature was also examined. We found that the conductance increases as a logarithmic function of time at 200 °C and that it increases steeply with increasing temperature until 500/600 °C where the rGO film decomposes.

Mobility and carrier density as functions of temperature were measured in Au-Si-doped GaAs. Because of inconsistency in the samples no conclusions were made with regard to the GaAs samples.

Dansk

Vi har målt flade- og kontaktmodstand i tynde film af termisk reduceret grafenoxid (rGO). Målingerne blev lavet ved hjælp af en Hallbar-struktur, hvilket ikke er gjort før. Flademodstanden blev bestemt til 120 kΩ, hvilket er meget højere end i grafen. Kontaktmodstanden blev bestemt til at være ubetydelig i forhold til flademodstanden ved stuetemperatur. Med RCDA (Resistance Curve Derivative Analysis) på en lille mængde data blev den dominerende transportmekanisme bestemt til at være Efros-Shklovskii VRH (Variable Range Hopping) med et vist bidrag fra Mott VRH.

På grund af problemer med at måle Hall-spænding stammende fra transportmekanismen i rGO blev mobilitet og ladningsbærertæthed ikke bestemt.

Konduktans in rGO som funktion af reduceringstid og temperatur blev også undersøgt. Vi fandt, at konduktansens stiger som en logarithmisk funktion af tid ved 200 °C, og at den stiger stejlt med temperatur indtil 500/600 °C, hvor rGO-filmen dekomponerer.

Mobiliteten og ladningsbærertætheden som funktion af temperatur blev målt i Au-Si-doteret GaAs. Grundet inkonsistens i prøverne blev der ikke draget nogen konklusion i denne sammenhæng.

2 Introduction

Graphene is an exciting new material with far better properties than those of silicon, which is the material of choice in electronic components today. Although graphene has better properties than silicon it is not yet used in the electronics industry because of the difficulty of producing it. The exfoliation method, which gives the best quality of graphene, is not viable industrially and so other techniques are needed.

One such method is the Hummers method [1] which yields graphene oxide (GO): one or more stacked layers of graphene with O- and OH-groups bond to some of the carbons. It is hoped that the right treatment (e.g., chemical, thermal) can reduce GO to rGO (reduced GO) and subsequently to graphene, thus establishing a way of synthesizing graphene.
Studies on the electric properties of rGO have already been made, e.g., [2], [3], [4]. However, its properties have yet to be determined using a Hall bar geometry. We examined this possibility as well as the effect of reducing it by thermal annealing.

In order to get to know the measuring equipment we also measured GaAs samples doped with Si and Au. There is, to our knowledge, no experimental evidence as to what effect Au-doping has on the properties of GaAs. Therefore, we want to measure the electric properties of Si-GaAs with and without Au to examine the effect of introducing Au.

Summarizing, we wanted to

1. Manufacture rGO Hall bars to be able to measure the electric properties of rGO.
2. Measure mobility, carrier density, contact resistance, and square resistance in an rGO film as functions of temperature and compare these quantities with those of graphene.
3. Analyze these quantities, hereby determining the conduction mechanism in rGO.
4. Measure total conductivity in an rGO film as a function of annealing temperature and time.
5. Measure mobility and carrier density in Si-GaAs with and without Au as a function of temperature and analyze the effect of introducing Au into Si-GaAs.

The entire project is made as a collaboration between Morten C. Hels and Thomas K. Andersen. Thus, sections are not labeled with the name of the author.

3 Theory

3.1 Structure of rGO

A graphite oxide single-layer sheet consists of a hexagonal, covalently linked carbon surface (like graphene) with oxygen-containing functional groups attached to various random sites, see Figure 1. Because the carbon bonds in the sheet are more stable than the bonds between carbon and oxygen-groups the latter will break more easily. Thus, when temperature is increased and more thermal energy is available some C-O and C-H bonds will break, leaving behind a purer carbon layer. When the rGO is annealed at constant temperature and increasing time it is expected

![Figure 1](image-url)
that the conductance will increase until it reaches a maximum when the remaining bonds require more thermal energy than is available.

### 3.2 Hopping Conductance

This subsection is based on [2], [6], [7], [8], and [9].

In a crystalline material electron states are delocalized because of translational invariance. This is the usual starting point for analysis of conduction. However, because of its heterogeneous structure rGO may not have available delocalized states at all energies. For convenience, a mobility edge $E_m$ can be defined so that states with $E < E_m$ are localized and states with $E > E_m$ are delocalized. If the temperature is sufficiently high that $E_F > E_m$ then conduction is undertaken primarily by carriers in delocalized states as usual. If, however, $E_F < E_m$ other mechanisms are relevant.

A first guess as to the resistance when $E_F < E_m$ is to give the thermal energy an exponential dependence so that the resistance $R$ satisfies

$$R \propto \exp \left( \frac{E_m - E_F}{k_B T} \right),$$

(1)

because fewer localized states are available at lower temperatures. The carriers tunnel through areas without available states. In order to tunnel, an overlap between the wavefunctions must be present. The wavefunctions decay exponentially with spatial separation in the tunneling region so an additional term can be added to give

$$R \propto \exp(-\alpha r_{ij}) \exp \left( \frac{E_m - E_F}{k_B T} \right),$$

(2)

where $\alpha$ is some constant and $r_{ij}$ is the separation between state $i$ and $j$. Several final states $j$ may be available for tunneling for a given initial state $i$ and so (2) becomes a sum over these states. Depending on the dimension of the system and whether the density of states at $E_F$ is assumed constant or not the final equation for $R$ is given as

$$R = R_0 \exp \left[ \left( \frac{T_0}{T} \right)^p \right],$$

(3)

where $T_0$ includes some constants, the density of states at the Fermi level, and a characteristic localization length. $p = 1, 1/2, 1/3, \text{and} 1/4$ correspond to the Arrhenius, 3D Efros-Shklovskii (ES), 2D Mott, and 3D Mott model, respectively. The approach as a whole is termed variable range hopping (VRH).

For practical purposes (3) can be used to determine the conduction mechanism in a material. This consist in fitting the value of $p$ which can be done quantitatively by introducing a dimensionless reduced energy $w$

$$w(T) = -\frac{d \ln(R)}{d \ln(T)} = p \left( \frac{T_0}{T} \right)^p$$

(4)

$$p(T) = -\frac{d \ln(w)}{d \ln(T)}.$$

(5)

Note that $p$ can depend on $T$ so that different conduction mechanisms may apply in different temperature intervals. Using this approach for modeling the data is called resistance curve derivative analysis (RCDA). An RCDA on our rGO samples is presented in the Results section.
3.3 Mobility and Carrier Density

Electron mobility is defined as

$$\mu = \frac{v_d}{E} = \frac{|e|\tau_m}{m},$$  \hspace{1cm} (6)

where $E$ is the magnitude of the electric field, $\tau_m$ is the momentum relaxation time, and $m$ is the mass of the electron. The last equality is true in the Drude model. Mathiessen’s rule gives a rough estimate of mobility as a function of temperature. In [10] it is stated as

$$\frac{1}{\tau_m} = \frac{1}{\tau_{im}} + \frac{1}{\tau_{ph}},$$  \hspace{1cm} (7)

where $\tau_{im}$ and $\tau_{ph}$ are the time between impurity and phonon scattering, respectively, and the two types of scattering are assumed not to interact. When the temperature goes down, the momentum relaxation time (and hence mobility) increases due to suppression of phonon scattering. When phonon scattering is so small that impurity scattering is the dominant factor, it does not increase any further. Thus, undoped samples can reach significantly higher mobilities than doped ones, although they also have fewer conduction electrons.

Carrier density $n$ is the concentration of occupied conduction states. For an intrinsic semiconductor this is equal to the concentration of electrons in the conduction band $n$ or, equivalently, the number of holes in the valence band $p$. Following the calculation in [10] we get

$$n = p = \int_{E_c}^{\infty} D_e(\epsilon)f_e(\epsilon)d\epsilon \propto T^{3/2} \exp\left(-\frac{E_g}{k_BT}\right),$$  \hspace{1cm} (8)

where $E_g$ is the band gap. (8) states that the carrier density decreases exponentially as the temperature is lowered and fewer carriers are excited thermally. Doping the semiconductor gives energy levels in the band gap, which provide easier access to conduction states.

3.4 Measuring resistance, mobility, and carrier density

Mobility and carrier density can be measured with so-called Hall bar measurements. A Hall bar (shown in Figure 2) can be seen as a rectangular conductor with a current running in the $x$-direction of the bar and a magnetic field $B$ in the $y$-direction. Due to the Lorentz force, charged particles moving in the $x$-direction will be deflected in the $\pm z$-direction depending on their charge. This causes a buildup of charge on one side of the bar, which leads to an electric field in the $z$-direction, measurable as the Hall voltage ($V_H$) across the bar. When the force, caused by the electrical field across the bar, is at equilibrium with the Lorentz force, the current-carrying charges, moving in the $x$-direction, experience no net force.

The Lorentz force is

$$\vec{F}_L = q\vec{v} \times \vec{B},$$  \hspace{1cm} (9)

and if we assume that the $B$-field is perpendicular to $\vec{v}$ and the charge is an electron we get

$$F_L = -ev_dB,$$  \hspace{1cm} (10)

where $v_d$ is the drift velocity. Now the electric field across the bar $E_z$ needs to cancel out this effect, so

$$-eE_z + F_L = 0.$$  \hspace{1cm} (11)
This result is used in the Drude model to give expressions for mobility $\mu$ and carrier density $n$ \cite{[11]}

$$\mu = \frac{I/|e|}{n_s V_x W/L}$$  \hspace{1cm} (12)

$$n = \frac{I/|e|}{dV_H/dB}$$  \hspace{1cm} (13)

where $V_x$ is the longitudinal voltage and $W$ and $L$ is the width and length of the bar. $V_x$ can also be used to determine the square resistance $R_s$ of the material. $R_s$ is independent of the contact resistance as $V_x$ is measured with different terminals than the ones carrying the current. Thus, $R_s$ is measured using four terminals while the total resistance $R_{tot}$, which also includes the resistance arising from the contact-material interface, is a two-terminal measurement. They are given as

$$R_s = \frac{V_x W}{L} \hspace{1cm} \text{and} \hspace{1cm} R_{tot} = \frac{V}{I}.$$  \hspace{1cm} (14)

The resistance of the entire bar $R_{sheet}$ (without the contact resistance) is calculated as $R_s \times s$ where $s$ is the number of squares in the Hall bar (2.6 in our case). Knowing $R_s$ and $R_{tot}$ we can calculate the contact resistance $R_c$ as

$$R_c = \frac{1}{2}(R_{tot} - R_{sheet}).$$  \hspace{1cm} (15)

The factor of one-half is necessary as our measurements always include two contact-material interfaces.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{hall_bar_diagram.png}
\caption{Left: A schematic representation of the Hall bar. From \cite{[12]}. Right: A Hall bar seen from the $y$-axis. A bias voltage $V$ is applied between the black boxes which causes a current $I$ to run. The boxes labeled $V_1, V_2, V_3$ are voltage-measuring terminals. From \cite{[11]}.}
\end{figure}

### 3.5 Schottky barrier

At a metal-semiconductor interface the contact resistance is caused by a Schottky barrier as shown in Figure 3. When the metal and the semiconductor is brought into contact a transfer of particles occurs as the Fermi energies must be equal at the intersection. For an $n$-type semiconductor, electrons are transferred from the semiconductor to the metal leaving positive charges behind, which lower the energy of the states in the semiconductor. As the energy of the
states in the metal and semiconductor must be equal at the intersection this causes a "bend" in the energy band. Electrons coming from the left must now climb the electrostatic potential of the electrons gathered at the metal-side of the contact before entering the semiconductor just as they must climb an equivalent barrier when exiting the semiconductor again.

Figure 3: Interface between an $n$-type semiconductor and a metal. The potential barrier formed in (c) is called a Schottky barrier. The broken line is the Fermi level. From [10].

4 Materials and Methods

4.1 Synthesis of rGO

rGO was synthesized using the modified Hummers method [1] as in [5] and [13]. Graphite powder, sodium nitrate, and sulfuric acid were stirred in an ice bath. Then potassium permanganate was gradually added as an oxidizing agent and the solution was kept at about 35°C for an hour to allow the reaction to proceed. Next, water was added which caused the temperature to rise to about 90°C. To stop the reaction water was added along with hydrogen peroxide which reduced the remaining permanganate. The resulting solution could then be centrifuged and filtered until visible particles had been removed, leaving a solution of GO.

4.2 rGO samples

Gold and platinum samples were made with UV-lithography. An overview of the process is shown in Figure 4.

We used a silicon wafer with a 300 nm thick top layer of SiO₂. The wafer was cut from a larger piece and cleaned in acetone and isopropanol (IPA) before application of resist. The resist (AZ4521) was applied by spin-coating for 45 seconds at 4000 rpm. Then the UV-lithography steps followed: Firstly, a mask was aligned and exposed to UV light for 8 seconds and developed in AZ400K so that resist was applied only on the areas that were not to contain metal. The exposure time had been calibrated in advance to minimize UV light leakage. The resulting resist thickness was ~2 μm. Secondly, the wanted metal (Au or Pt) was evaporated onto the entire wafer and the photoresist, where an excess layer of the metal was located, was removed with acetone and IPA. This left us with a metal Hall bar pattern ready for an addition of GO or rGO (Figure 5).
The samples made with Au got rGO on it. The rGO had, before addition to the samples, been annealed for 45 minutes at 600 °C in a 4 mL/min N₂ atmosphere on a bare Si wafer. To remove the rGO flake from the Si wafer a drop of NaOH was dripped on it. When the NaOH droplet slid off the sample, the rGO flake could be lifted off in H₂O as seen in Figure 6a. The flake could hereafter be transferred to the aforementioned ready-made sample by dragging the sample carefully up into the floating rGO flake. When the rGO was on the sample, a thin film of H₂O was between the sample and the flake. To remove as much of this film as possible the sample was vacuum-annealed in 10⁻² mbar for 1 hour at 30 °C. The flakes had dimensions of 3 mm x 3 mm to 1.5 mm x 1 mm and thus covered 2-6 Hall bars on a single wafer. This procedure was only made on our Au samples. On the Pt samples the GO was not reduced before.
it was transferred to the samples. Here the reduction of the GO was made sequentially, which is described in Subsection 5.4. To improve the contact between electrodes and rGO we annealed the sample at 185°C for 5 min.

**Figure 5:** Left: An Au sample before processing of rGO. Middle: The same Hall bar after processing, ready for measurement. The rGO is visible as dark areas on the brown background of SiO$_2$ as well as on the gold electrodes. Right: Magnified view of the middle image. The overlap in the bottom right corner is of no concern as the gate electrodes were not used.

**Figure 6:** (a): rGO flake (left of the dark square wafer). (b): Averages of AFM cross sections showing thickness of rGO film. The thickness was not constant within a sample. The rGO samples measured here had been annealed for 600°C for 45 minutes.

Before further processing the thickness of the rGO film was measured. Profile images are shown in Figures 6b and 7. The thickness was measured to 3-7.9 nm for annealed Au samples and 7-10 nm for annealed Pt samples. The thickness varied within a single sample.

Again, the samples were spin-coated for 45 seconds at 4000 rpm before they were exposed to UV light through a mesa mask, and developed in AZ400K in order to obtain protective photoresist on top of the rGO that were to constitute the Hall bars. The entire samples were then ashed for 210-705 seconds (the time to remove the excessive rGO was different for each sample) to remove the non-Hall bar rGO. When this was accomplished, the remaining resist was
removed with acetone and IPA. Following this step the samples were ready for measurements. A functioning rGO Hall bar on an Au sample is shown in Figure 5. An overview of all GO samples prepared is shown in Table 2 in Appendix A.

The first few samples that we prepared deviated slightly from this procedure. The deviation originated from misalignment of the second mask which had to be removed with PG remover (sample B) or acetone (samples A5 and A7). Exposing the rGO to resist and acetone/PG remover twice instead of once on these samples may have had an impact on its properties as indicated in Figure 15 in which the resistance of sample B is consistently higher than that of the other samples.

Summing up, two types of samples were prepared: Some with Ti/Au contacts and some with Ti/Pt contacts. The former had 120 nm Au (deposition rate: 1-1.5 Å/s) on top of 15 nm Ti (2-3 Å/s) while the latter had 120 nm Pt (0.2-2.1 Å/s) on top of 12 nm Ti (1 Å/s).

In order to make the Au samples ready for measurement they were glued to ceramic chip carriers with epoxy glue and were bonded with gold threads from the Ti/Au contacts to the chip carriers’ contacts. To be able to apply gate voltage some of the samples were glued with silver paste to chip carriers with a gold bottom surface and were bonded as before as well as to the gold surface at the chip carrier. The silver paste ensured contact between gold surface and sample and any voltage supplied to the gold surface would thus transfer into the Si-layer of the sample and be separated from the rGO only by the 300 nm top SiO$_2$ layer. The Pt samples were not bonded because the measurements on them were performed at a probe station.

A third mask existed that was designed to remove rGO from the electrodes to facilitate better contact between bonding thread and electrode. As the bonding was never a problem the third mask was not used to avoid further alignment issues.

4.3 Measuring equipment

To perform Hall measurements on our samples we used a cryocooler. An overview of its electrical components is shown in Figure 8. This cooler works in principle as a refrigerator, compressing and expanding a coolant, which in this case is helium. The cooling process works by compression of helium in the compressor at room temperature, the gas is then cooled by passing through a water-cooled heat exchanger. The compressed gas is then led to the the cold-head, consisting of two stages, for expansion. The expanding helium cools down the first stage in the cold-head to \(~80\) K and afterwards down to \(~10\) K, the so-called sample stage. The gas is then led back to the compressor for another cycle [14]. A typical temperature sweep down takes about 2 hours. To obtain these cold temperatures vacuum is necessary. A vacuum pump is attached to the
system and can maintain a rough vacuum of ∼4-10 mTorr.

Figure 8: Left: Electrical connections for sample (shown in grey), voltmeter, and current source to the switch-matrix. Right: An overview of the experimental setup. Both from [14]

The data acquisition is controlled by a PC using a Labview program (described in [14]). The PC communicates with the instruments via a National Instruments BNC-2110. The instruments for measurements consist of a HP3478A voltmeter, with a resolution of 100 nV, the current is supplied by a Keithley 224 DC current source, typically applying ±10 µA. The sample is connected to the current source and voltmeter through a Keithley 705 switch-matrix, shown in Figure 8. This switch-matrix connects the sample to the instruments in a flexible way. Furthermore, the National Instruments BNC-2110 controls the Lakeshore 330 temperature readout and the PSC 44M magnet controller. This magnet controller is an interface box connecting the National Instruments BNC-2110 with a bipolar magnet power supply, which at full scale can reach a $B$-field on ±0.45 T. In our measurements we usually applied ±0.3 T, the exception being ±0.4 T in the Hall voltage vs magnetic field measurement (Subsection 5.3).

5 Results and Discussion

Before presenting the central RCDA some auxiliary measurements are shown. The RCDA itself consists of an unsuccessful part regarding $R_s$ and a successful part regarding $R_{tot}$.

5.1 Sheet and Contact Resistance in rGO

The contact resistance was measured at room temperature at 1) the Hall bars and 2) the Transfer Length Method (TLM) electrodes.

At the Hall bars the total resistance $R_{tot}$ from one contact to another was measured manually with a multimeter and compared with the calculated sheet resistance $R_{sheet}$ for which the $R_s$-values from Figure 15 were used. If the rGO film is treated as a semiconductor (this is examined in Subsection 5.2) the contact resistance arises from a Schottky barrier as described in the theory section. The results are shown in Table 1.

The TLM electrodes on our samples were separated by 10, 20, 40, 80, 160 and 320 µm, respectively. The width $W$ of the rGO at the TLM electrodes was 160 µm where the rGO film was not tattered. Due to the location of rGO, only some TLM electrodes on sample C were available for measuring. Only adjacent electrodes were measured to avoid introducing more than two contact resistances. The data is shown in Figure 9. The intercept represents $2R_c$ and so we
<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_{tot}$</th>
<th>$R_s$</th>
<th>$R_{sheet}$</th>
<th>$R_c$</th>
</tr>
</thead>
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<tr>
<td>A5</td>
<td>0.319</td>
<td>0.100</td>
<td>0.260</td>
<td>0.0295</td>
</tr>
<tr>
<td>A7</td>
<td>0.403</td>
<td>0.179</td>
<td>0.465</td>
<td>-0.0312</td>
</tr>
<tr>
<td>B</td>
<td>0.843</td>
<td>0.2815</td>
<td>0.7319</td>
<td>0.0556</td>
</tr>
<tr>
<td>C4</td>
<td>0.338</td>
<td>0.120</td>
<td>0.312</td>
<td>0.013</td>
</tr>
<tr>
<td>C6</td>
<td>1.9</td>
<td>0.0937</td>
<td>0.2436</td>
<td>0.8282</td>
</tr>
<tr>
<td>C7</td>
<td>0.273</td>
<td>0.109</td>
<td>0.2834</td>
<td>-0.005</td>
</tr>
<tr>
<td>C8</td>
<td>0.236</td>
<td>0.075</td>
<td>0.195</td>
<td>0.0205</td>
</tr>
</tbody>
</table>

Table 1: Hall bar contact resistance $R_s$ for Au samples at $T = 300\,\text{K}$. All numbers are in MΩ.

![Figure 9](image-url) **Figure 9:** Plots for determination of contact resistance $R_c$. $L$ varied from 10 – 320 µm. $W = 160\,\mu\text{m}$.

find that $R_c = -0.011, 0.0085$ and $0.004\,\text{MΩ}$, respectively. Disregarding the negative $R_c$ of TLM A, this is somewhat smaller than the $R_c$ found at the Hall bars, perhaps because the overlap between Au and rGO is smaller at the Hall bars. The $R_s$ of TLM A is higher than the Hall bar $R_s$ which is explained by a more tattered rGO film as seen by comparing Figures 10 and 5. Conversely, TLM B and C have $R_s$ of the same order of magnitude or lower than the hall bar $R_s$ which corresponds to a better quality of rGO than TLM A in Figure 10. Although the right-most electrodes of TLM C appear to be connected with rGO we were not able to measure any current between them.

Overall we find that the contact resistance is negligible compared to the sheet resistance. To examine the nature of the contact resistance we performed gate sweeps on the Hall bars.

### 5.2 Gate Sweeps on rGO

To examine the character of the energy landscape in rGO gate sweeps were performed. Two limits can be put on the dispersion relation of rGO: 1) the Dirac cone of pristine graphene which has a vanishing density of states at the Dirac points and 2) a location dependent disordered relation caused by heterogeneous insulating and conduction areas. Mixing these two pictures gives somewhat defined conduction and valence bands with a number of states in-between. For this dispersion the current through the sample will be lowest somewhere between the conduction
**Figure 10:** Three microscope images of TLM A, B and C (top to bottom) brought together in one image with enhanced contrast. The dark lines across the picture are bonding threads and red lines show rGO position. The lines on the electrodes themselves are caused by the probing needles. Note the holes in the rGO film shown as areas enclosed in red lines. TLM A has more holes which may account for its higher sheet resistance.
and valence band where the density of states is lowest.

Voltage was supplied to the chip carrier gold surface, which was connected with the sample as described in Materials and Methods. In this way we were able to control the gate voltage and shift the Fermi energy.

Gate sweeps at 300 K and 150 K are shown in Figure 11. There is some hysteresis in the measurement, possibly due to adsorption of water molecules as in [15]. For both temperatures the charge neutrality point lies at negative voltages. The presence of a peak indicates that there is, indeed, an interval in the energy landscape that can accomodate less charge carriers, i.e., it has a lower density of states. The y-scales on the gate sweeps is also worth taking into account. Considering the relatively large sweep range the change in resistance is not very big. This signifies that the density of states does not vary very much. This is in contrast to pristine graphene which has a sharper peak (see [16]). The gate sweeps show that the rGO does have some sort of band gap, which contributes to the interpretation of a Schottky barrier in the metal-rGO interface as the cause of the contact resistance.

After a couple of gate sweeps at $V_g \sim 50$ V had been performed the current changed character from near-parabolic (as in Figure 11) to linear, indicating gate leakage. This is the reason for the small amount of gate sweep data.

Gate sweeps at low temperature $\sim 10$ K were also attempted. Strangely, gate leakage seemed to be more prominent at low $T$ resulting in linear $I-V_g$ plots. Also, the measuring equipment was not always able to maintain a constant temperature below about 20 K. In the samples that had discontinuities at low $T$ this resulted in large variations in $R_s$ over the course of a single sweep ($\sim 25$ seconds) because of the steep $R_s$ vs. $T$ slope at low $T$. An instant change in $T$ of 1 K was not unusual. In one measurement of C4, e.g., this corresponds to a relative change in $R_s$ of 15 %.

We have seen that rGO has some sort of band gap. In the next subsection we explore whether this translates into a temperature-varying carrier density as we expect from a semiconductor.

### 5.3 Mobility and Carrier Density

Mobility and carrier density were measured using the Hall bar geometry and calculated with (13) and (12). However, the measurement turned out to be difficult. As shown in Figure 12 the initial measurements are not definitive.

We make a second attempt at measuring the Hall voltage by sweeping the $B$-field. In the
main Hall bar program the $B$-field is set to a specific value where $V_H$ is measured. The ratio is then used as $dV_H/dB$ which is allowed if the correlation is linear. By sweeping the $B$-field we hoped to get a better approximation of $dV_H/dB$ than by measuring a single point because the noise would be averaged out. For this purpose a Labview program (shown in appendix C) was written which gave the results shown in Figure 13. It is obvious that the rGO sample does not show a clear relationship between $V_H$ and $B$ compared to the GaAs samples. The rGO sample measured here was the most probable to show the desired relationship. As even this sample gave ambiguous results we decided not to pursue measuring mobility and carrier density further. It would be interesting, though, to see if an averaged $dV_H/dB$ would give consistent results for mobility and carrier density.

One possible explanation for $V_H$ not being uniquely measureable is the direction of the current. Because rGO is heterogeneous it will have regions with varying resistivity. The charge carriers will move along the direction of least resistance which will not always be in the longitudinal direction of the bar. The path of least resistance will change or widen with the applied voltage to be able to accomodate increasing current. Then the Lorentz force will not point in the transverse direction at all points and $V_H$ will change accordingly. This scenario differs from the regular scattering picture in that the majority of charge carriers move along the same path rather than being scattered randomly.

These considerations show that we should be careful in treating rGO like a conventional semiconductor. It might have an energy interval with a lower density of states, but that does not mean that it resembles a semiconductor in other ways. Indeed, a band gap presupposes a $k$-space that in turn requires translational invariance, which for rGO can only be achieved approximately at best.

Although this exercise turned out to be a dead end, we did get confirmation that the $V_H$ vs. $B$-field relationship was exactly linear for the GaAs samples and thus that the calculations made in the main Hall bar measuring program were justified in this case.
Figure 13: $V_H$ vs $B$-field measurement for an rGO (red) sample and a GaAs (blue) sample. The scale on the left hand side is for the rGO sample. The GaAs measurement gives a clear correlation between $V_H$ and $B$. Although a slope can be inferred from the rGO measurement the points do not pass through $(B, V_H) = (0, 0)$ which they should. Note also the small scale on the rGO $y$-axis.

5.4 Effect of Thermal Annealing on Resistance

In order to examine the thermal annealing effect on the GO film we annealed the Pt samples in steps, measuring conductance in-between at room temperature. The reduction was done 1) with constant temperature and increasing time in steps of 5 minutes and 2) with constant time of 50 minutes and varying temperature. The data for the time-varying and temperature-varying reduction is shown in Figures 14a and 14b, respectively. All annealing was done in an atmosphere of $N_2$ at a flow of 4 mL/min.

When annealed with constant temperature and increasing time the samples show a clear improvement in conductance as they are reduced. The data was fitted to logarithmic expressions of the form

$$G = G_0 \ln(t/t_0),$$

with $G_0$ as the conductance at $t = e \cdot t_0$. This yielded $G_0 = 2.985 \cdot 10^{-8}$ S, $t_0 = 0.3569$ min for A2 and $G_0 = 4.5085 \cdot 10^{-8}$ S, $t_0 = 0.3793$ min for A4. The data was fitted linearly in $t$ as $\ln(G/G_0) = t/t_0$ which gave $r^2$-values of 0.997 and 0.993, respectively. As expected the conductance increases until the remaining bonds require more thermal energy to break.

Reduction with constant time and variable temperature is shown in Figure 14b. The same sample was heated for 50 minutes at one temperature, then at 50 minutes at $100^\circ C$ higher and so on. The total reduction time for the sample is thus 250 minutes which is probably the reason why this sample decomposes at $500/600^\circ C$ (giving $G = 0$) when the Au samples with 45 minutes of total reduction time do not. As expected, conduction increases steeply with temperature as more thermal energy is available to break C=O, C-O and C-H bonds. The decomposition at 500/600$^\circ C$ is surprising, comparing with the results from [4] in which rGO was annealed at up to $1100^\circ C$ without decomposing.
Figure 14: (a): Conductance in rGO on Pt samples vs. reduction time at 200°C. Prior to these measurements the rGO film was annealed for 10 minutes at 185°C and processed as described in Materials and Methods. (b): Same as (a) with constant time (50 minutes) and variable temperature.

5.5 Resistance Curve Derivative Analysis

The temperature dependence of square resistance $R_s$ was measured with four terminals on the Au samples. The results are shown in Figure 15. As expected, $R_s$ increases with decreasing $T$ as the thermal energy is lowered. The resistance is within 1-2 orders of magnitude of the results from [7] (chemically reduced GO) and [3] (hydrogenated graphene). At room temperature $R_s$ is slightly higher than 120 kΩ which is large compared with graphene at about 0.5 kΩ [16].

It should be noted that the $I$-$V$ relation at low $T$ is non-ohmic as shown in Figure 16. Thus, the $R_s$ data for low $T$ is not a valid representation of the actual $R_s$ which varies with voltage.

To model the data we attempted an RCDA which was successfully applied to rGO data in [2], [3], and [7]. The data was imported into Mathematica and an approximate function was fitted with the built-in Interpolation command. The constructed approximate function was differentiable and thus allowed us to apply equations (4) and (5) quantitatively. As the samples exhibited similar behavior (as shown in Figure 15) only some were analyzed. For these samples a reasonably well-behaved slope was obtained for $T = 20$-150 K but the data was often too noisy outside this interval to be immediately analyzable when differentiated. For $T = 20$-150 K this method yielded $p \approx -0.28$ and $p \approx -0.75$. Referring to the models mentioned in the theory section, these values are not too bad but for the minus sign which is explained in Figure 17a: The lower part of the red $R_s$ curve has a negative second derivative (from Equations (4) and (5)) which gives the wrong sign of $p$. It also has a discontinuity at $\ln(T) \approx 3.5$ which further impedes its use in analysis.

It was tested if connecting and removing the vacuum pump from the system or knocking gently on the sample holder had any relation to the discontinuities. Also, the raw data was examined in order to find out if the discontinuities occurred when the current source reached its maximum voltage output. No correlation was found in either case.

For high temperatures (>150 K) some $R_s$ data was analyzable to give a meaningful value of $p$. One such sample gave $p = 0.25$ for high $T$ which is about the value that the VRH models predict.

Also shown in Figure 17a, however, is the total resistance $R_{tot}$ measured with two terminals.
Figure 15: Square resistance measured against $T$. Dashed lines indicate that the measurement is made with $T$ sweeping down. The opposite is true for solid lines. The figure is meant to illustrate the homogeneity in the samples. The slightly higher $R_s$ on sample B could originate from photoresist removal with PG remover.

Figure 16: Source-drain voltage sweep. Dashed lines have $V_{sd}$ sweeping from high to low voltage. The current clearly does not depend linearly on $V_{sd}$ at low temperature. Measurements were also made at 20, 30 and 40 K (not shown) which exhibit a gradual straightening of the curve with increasing temperature. The data is from sample C4.
Figure 17: (a): Semilog plot of resistance $R$ vs. $\ln(T)$ which demonstrates the slope from equation (4). The discontinuity in $R_s$ and its negative second derivative make it unsuitable for analysis. $R_{tot}$, on the other hand, is quite well-behaved. (b): Semilog plot of total resistance $R_{tot}$ vs $T^{-1/2}$ (top x axis) and $T^{-1/3}$ (bottom x axis). Although similar, the ES fit seems to be slightly better than the Mott fit because its curve is straighter. The sample measured is C4.

in the same temperature sweep. This curve was analyzable as it has a positive second derivative and no discontinuity. It is plotted in Figure 17b against $T^{-1/2}$ and $T^{-1/3}$ corresponding to ES and 2D Mott fit, respectively. From (5) this should yield a straight line for the correct mechanism (exponent). Thus, the ES fit seems to be slightly better than the Mott fit. The exponent can also be determined from the slope of the curve in Figure 18. In this figure it becomes clearer that different mechanisms could be applicable in different regions. The data from $\ln(T) \approx 3.25$ and up can be fitted to a slope ($p$-value) of 0.56. It appears that the slope changes slightly at $\ln(T) \approx 4.5$. Using this as a separation point for two different linear fits gives $p \approx 0.77$ and $p \approx 0.38$ for the low and high part, respectively. As the resistance is non-ohmic below $T \sim 50\,K \Rightarrow \ln(T)\sim 4$ the validity of the 0.77 slope is questioned. This leaves us with slopes of 0.38 and 0.56 which are evidence that the conduction mechanism in rGO is VRH with ES as the dominant mechanism. This conclusion is also reached in [3]. Because $R_{tot}$ was measured only one time, note that this conclusion is based on a single temperature sweep only. Considering the homogeneity of the samples it is likely to hold for them all.

With $R_{tot}$ fitting our expectations and $R_s$ not being analyzable at all we must question the validity of the $R_s$ measurement. Figure 17a makes an important point in this respect: As the difference between $R_{tot}$ and $2.6 \times R_s$ is equal to $2R_c$ we would expect the contact resistance to have a transition equal and opposite to $R_s$ at the discontinuity at $\ln(T) \approx 3.5$ so as to hold $R_{tot}$ constant. This does not seem likely. Furthermore, as VRH describes a phenomenon in the sheet—and not the interface—we should be able to fit $R_s$ better or at least just as well as $R_{tot}$. Clearly, this is not the case. With the cause of the discontinuities still unresolved we are led to the important conclusion that the $R_s$ data is not trustworthy at medium to low temperatures. They do seem to be valid at room temperature, though. This is surprising considering the consistency with which the GaAs samples were measured (see Subsection 6.3).
**Figure 18**: Plot of $-\ln(w)$ vs $\ln(T)$. $p$ is given from (5) as the slope of this graph. The discontinuity at $\ln(T) = 5$ and data below $\ln(T) = 3.3$ were removed when the fit was made. Straight lines show different interpretations of the data. The interval from 3.3-5.7 can be fitted as one to give ES-type behavior but the interval can also be fitted as two parts to give a Mott-like fit in the high end, and a third, unknown fit in the low end. The data is from sample C4.
6 Au-Si-doped GaAs

6.1 Theory

Silicon introduced in GaAs can be expected to either substitute the Ga or the As atoms. This will create an n-type or p-type semiconductor, respectively, as Si has one electron more than Ga and one fewer than As. The ratio between the Ga- and As substitutions \([\text{Si}_{\text{Ga}}]/[\text{Si}_{\text{As}}]\) depends on several factors, e.g., growth temperature and crystal growth plane [17]. Our samples were n-type.

Apart from the Si atoms Au is also introduced as a dopant. One approach to determining its effect on the properties is to treat the Au atoms as a conventional dopant which will be an acceptor impurity in the attempt to obtain the same bond configuration as Ga or As. The number of holes provided will be 2 if the Au substitutes a Ga atom and 4 if it substitutes an As atom. With Si providing electrons and Au trapping them, one would expect the carrier density to decrease in Si-doped GaAs if Au were introduced.

As Au is an impurity in the GaAs lattice it can be predicted to decrease momentum relaxation time \(\tau_m\) and hence from (6) also decrease mobility \(\mu\).

6.2 Experimental

Six GaAs samples were manufactured to be 3 micrometer thick - four doped with Au and two without. The growth rate (GR) was 0.96 \(\mu\)m/hr for NBI 607, NBI 608, and NBI 624. Furthermore, all six samples were doped with \(10^{21} \text{m}^{-3}\) Si as well as the As-pressure was \(8.3 \cdot 10^{-6}\) Torr and the Ga-pressure was \(3 \cdot 10^{-7}\) Torr. The samples NBI 607 and NBI 608 were almost identical, but NBI 608 was co-doped with Au. When NBI 721 was made the Ga source was changed from the previous growth to 0.9 \(\mu\)m/hr. NBI 624, NBI 714 and NBI 722 were doped with Au. NBI 624 and 608 were doped at 807 \(^\circ\)C and the two remaining samples were doped at 900 \(^\circ\)C. An overview of the samples is shown in Table 3.

6.3 Results

Looking at the carrier density graph in Figure 19, no clear correlation occurs. Nevertheless, NBI 721 is significantly different from the other samples. It has half the carrier density of NBI 722. The Au-doping would, seen from a theoretical point of view, create a deep level in the ‘forbidden’ gap between the valence band and the conduction band. Firstly, this deep level will compensate shallow dopants and, as a consequence, reduce the carrier density. A resultant effect of this is a reduction of the mobility, since the concentration of the charged levels increases when the carrier density decreases [18]. The samples are all n-type doped and would, therefore, give rise to less charge carriers, due to the deep levels that would ‘catch’ some of the electrons - but the opposite happens. It is impossible, based on this data, to conclude on this, but perhaps a higher concentration of Au would fit in the expected picture.

Looking at the mobility graph, NBI 721 and NBI 722 fit in the aforementioned expectation. This is the only data that fits our expectation. NBI 721’s significantly lower carrier density could be because of the Ga source change, that gives it different properties from NBI 607 and NBI 608, which were made with the old Ga source.
Figure 19: Mobility and carrier density for the GaAs samples plotted against temperature. Dashed lines indicate sweep from high to low $T$. No clear conclusions can be made from this data as the Au samples do not exhibit consistent behavior relative to the samples without Au.
7 Summary

7.1 Conclusion

Referring to the points stated in the introduction we conclude the following:

1. rGO Hall bars were successfully manufactured using UV lithography.

2. The Hall voltage was difficult or impossible to measure because of the localized and percolative conduction mechanisms in rGO. Thus, mobility and carrier density were not determined. Sheet resistance was determined to about 120 kΩ at room temperature which is far from graphene at 0.5 kΩ. Contact resistance was negligible compared to sheet resistance at room temperature.

3. The conduction mechanism was determined to be VRH with ES as the dominant mechanism. Note that this conclusion is based on a small amount of data.

4. The total conductivity vs. reduction time was fitted with very high precision as a logarithmic function at 200 °C. The total conductivity was found to increase steeply with reduction temperature until 500/600 °C where the rGO film decomposed.

5. Because of inconsistencies during processing no conclusions were made with regard to the GaAs samples. The tendency that might be forced upon the data contradicted the predictions but could just as well originate in processing differences between the samples.

7.2 Outlook

Concluding our project we suggest the following subjects to be pursued in future studies:

1. Generate valid square resistance measurements to be able to find the contact resistance as a function of temperature.

2. Sweep the B-field to obtain an averaged dV_H/dB and use it to calculate mobility and carrier density.

3. Make more annealing measurements. Is it generally true that our rGO film decomposes at 500/600 °C?

4. Measure resistance, mobility, and carrier density (if point 2 is achieved) as functions of temperature at different reduction stages.
Appendices

A  rGO Samples

<table>
<thead>
<tr>
<th>Name</th>
<th>Electrode material</th>
<th>Electrode height</th>
<th>Dep. rate</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>A5</td>
<td>Au</td>
<td>120 nm</td>
<td>1-1.5 Å/s</td>
<td>Misalignment. Resist-removal with acetone.</td>
</tr>
<tr>
<td>A7</td>
<td>Au</td>
<td>120 nm</td>
<td>1-1.5 Å/s</td>
<td>Misalignment. Resist-removal with acetone.</td>
</tr>
<tr>
<td>B</td>
<td>Au</td>
<td>120 nm</td>
<td>1-1.5 Å/s</td>
<td>Misalignment. Resist-removal with PG remover</td>
</tr>
<tr>
<td>C3</td>
<td>Au</td>
<td>120 nm</td>
<td>1-1.5 Å/s</td>
<td></td>
</tr>
<tr>
<td>C4</td>
<td>Au</td>
<td>120 nm</td>
<td>1-1.5 Å/s</td>
<td></td>
</tr>
<tr>
<td>C6</td>
<td>Au</td>
<td>120 nm</td>
<td>1-1.5 Å/s</td>
<td></td>
</tr>
<tr>
<td>C7</td>
<td>Au</td>
<td>120 nm</td>
<td>1-1.5 Å/s</td>
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<td></td>
</tr>
<tr>
<td>D</td>
<td>Au</td>
<td>120 nm</td>
<td>1-1.5 Å/s</td>
<td>No functional Hall bars</td>
</tr>
<tr>
<td>Pt A2</td>
<td>Pt</td>
<td>120 nm</td>
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<td></td>
</tr>
<tr>
<td>Pt A4</td>
<td>Pt</td>
<td>120 nm</td>
<td>0.2-2.1 Å/s</td>
<td></td>
</tr>
<tr>
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<td>Pt</td>
<td>120 nm</td>
<td>0.2-2.1 Å/s</td>
<td></td>
</tr>
<tr>
<td>Pt C</td>
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<td>0.2-2.1 Å/s</td>
<td></td>
</tr>
<tr>
<td>Pt D</td>
<td>Pt</td>
<td>120 nm</td>
<td>0.2-2.1 Å/s</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Samples with the same letter and same electrode material have the same flake of rGO. The numbers refer to specific Hall bars on the wafers.

B  GaAs samples

<table>
<thead>
<tr>
<th>Batch no.</th>
<th>Growth and growth rate</th>
<th>Gold</th>
<th>Doping</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBI 607</td>
<td>3 μm GaAs (0.96 μm/hr)</td>
<td>No</td>
<td>Si $10^{21}$ m$^{-3}$</td>
</tr>
<tr>
<td>NBI 608</td>
<td>3 μm GaAs (0.96 μm/hr)</td>
<td>Yes</td>
<td>Si $10^{21}$ m$^{-3}$, $T_{Au} = 807°C$</td>
</tr>
<tr>
<td>NBI 624</td>
<td>3 μm GaAs (0.96 μm/hr)</td>
<td>Yes</td>
<td>Si $10^{21}$ m$^{-3}$, $T_{growth} = 711°C$, $T_{Au} = 807°C$</td>
</tr>
<tr>
<td>NBI 714</td>
<td>3 μm GaAs (0.9 μm/hr)</td>
<td>No</td>
<td>Si $10^{21}$ m$^{-3}$, $T_{growth} = 711°C$, $T_{Au} = 900°C$</td>
</tr>
<tr>
<td>NBI 721</td>
<td>3 μm GaAs (0.9 μm/hr)</td>
<td>Yes</td>
<td>Si $10^{21}$ m$^{-3}$, $T_{growth} = 711°C$, $T_{Au} = 900°C$</td>
</tr>
<tr>
<td>NBI 722</td>
<td>3 μm GaAs (0.9 μm/hr)</td>
<td>Yes</td>
<td>Si $10^{21}$ m$^{-3}$, $T_{growth} = 700°C$, $T_{Au} = 900°C$</td>
</tr>
</tbody>
</table>

Table 3: The GaAs samples measured. All samples, except NBI714 and NBI721, consisted of two Hall bars on a single chip carrier. Samples NBI714 and NBI721 consisted of four Hall bars on two separate chip carriers.
C  Labview program for Measuring $V_H$ with varying $B$-field

Figure 20: Labview program for measuring Hall voltage $V_H$ while sweeping the $B$-field. The two windows at the bottom are step 1 and 2 in the sequence with the yellow box in the upper part. Step 0 sets the $B$-field to the appropriate value in the $i$’th iteration while step 1 and 2 measures the voltage on either side of the Hall bar ($V_1$ and $V_2$). These values are subtracted and exported to the plotting and file appending commands (the part around the purple wires in the main window). The constant bias voltage is set by the user in the left part of the main window.
References


