Electron transport and carrier scattering in graphene

0. INTRODUCTION

The goal of this lab is to study electronic transport in graphene, a single layer of carbon. You will measure the most important transport parameters of this material: intrinsic doping level, charge carrier mobility, and minimum conductivity. You will understand the relation of these parameters to unusual physical properties of Dirac-like Hamiltonian of graphene. Furthermore, you will experimentally determine the dominant sources of scattering in graphene: defect scattering and phonon scattering. Finally, you will examine the contribution of quantum interference effects to transport in graphene. To carry out these measurements, you will get to know the basics of multiprobe measurements, learn lock-in operation, and acquire familiarity with low-temperature and high-vacuum techniques.

1. THEORY

1.1 Semiclassical transport

How does current flow in a conductive material? The simplest answer to this question was obtained in 1900 by Paul Drude using a classical electron gas approximation. Consider electrons (with mass m and charge e) placed in a uniform electrical field E. Assuming that the electrons undergo collisions with rate τ^{-1}, that completely randomize their velocity, we find the average electron "drift" velocity:

$$v_d = \mu E = \frac{e\tau}{m} E \qquad (1)$$

Here, $\mu = e\tau/m$ is the charge carrier mobility with units m^2/Vs, describing the response of carriers to an external electric field. It is now easy to show that the conductivity of the electron "gas" with density n is given by:

$$\sigma = v_d n = ne\mu = \frac{ne^2\tau}{m} \qquad (2)$$

That is the Drude formula. It was derived assuming that electrons are fully classical and behave as billiard balls hitting static atoms. Of course, these approximations are not fulfilled in realistic materials. Nevertheless, a very similar expression can be derived from the semiclassical Boltzmann transport equation that rigorously accounts for quantum mechanical scattering:

$$\sigma = \frac{ne^2\tau}{m^*} \qquad (3)$$

The only difference from the Eq. 2 is that instead of bare electron mass m, the effective mass $m^{*-1} = \hbar^{-2}\partial^2 E/\partial k^2$ (here $E(k)$ is the dispersion relation) is used. Despite its simplicity, the Eq. 3 is broadly used to describe transport of electrons and holes in a wide range of materials and devices.

The information about carrier scattering is "encoded" in Eq. 3 through the scattering time τ. These are the main sources of scattering:

- **Defect/Impurity scattering.** Any distortion of the crystal order (e.g. a missing atom) or external charges (e.g. impurities or dopants) violate translational invariance of the crystal and cause scattering. The corresponding scattering rate $(\tau_{defect})^{-1}$ is roughly temperature-independent.

- **Phonon scattering.** Charge carriers can also be scattered on the periodic distortion of the crystalline ordered caused by phonons. Short-wavelength optical phonons are the dominant scattering source. As phonons are excited predominantly at elevated temperatures, the scattering rate $(\tau_{phonon})^{-1}$ increases with temperature.

Multiple scattering mechanisms simultaneously present in a sample are accounted for through a semi-empirical Matthiessen rule. The rule states that resistivity contribution from different scattering mechanisms simply add up. In terms of scattering times entering in Eq. 3,

$$\tau^{-1} = (\tau_{defect})^{-1} + (\tau_{phonon})^{-1} \quad (4)$$

It is important to understand the approximation inherent in Eq. 3. While the equation is semiclassical, it does account for the bandstructure (through the effective mass) and complex scattering potentials (through τ). It is assumed, however, that both τ and m are momentum- and direction- independent. The relaxation time approximation used in deriving Eq. 3 assumes that the drift velocity is much smaller than the Fermi velocity, $v_D << v_F$. That approximation breaks down only in the cleanest of samples and in the highest of fields. Finally, Eq. 3 does not account for quantum interference between multiple scattering events. Such interference gives rise to low-temperature phenomena such as weak localization and universal conductance fluctuations.

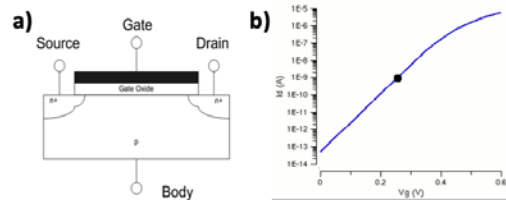### 1.2 Field Effect and Field Effect Transistors

One of the interesting applications of the Drude formula (Eq. 3) is to describe the operation of one of the pillars of modern electronics, the Field Effect Transistor (FET). The FET is an electronic device, which uses electric field to modulate the flow of an electric current (Fig. 1a). The current flows through a thin layer of semiconducting "channel" between the so-called "source" and "drain" electrodes. An

Fig. 1 a) A schematic drawing of Field Effect Transistor (FET) **b)** Current-voltage response of a FET (from *Wikipedia*)

external "gate" voltage V_G is applied between the channel and the "gate" electrode thus inducing an electric field. The gate electrode is separated from the channel by a thin insulating layer that is characterized by an areal capacitance C. A charge carrier density in the channel, induced by V_G, is given by:

$$n = CV_G/e \quad (5)$$

Finally, the conductivity of the channel changes in response to V_G, according to the Eq. 3. When the carriers are fully depleted from the channel ($n=0$), the transistor "turns OFF". A current-voltage characteristic I-V_g of a typical FET is show in Fig. 1b.

Metal-Oxide-Semiconductor FETs (MOSFETs) are the most common element in modern electronics. These are the most important characteristics of a FET:

- **Carrier mobility.** Carrier mobility of a material used for FETs determines the amount of heat dissipated in a transistor. For Silicon, the carrier mobility at room temperature cannot be higher 1,000 cm^2/Vs even for impurity-free material. That value is limited by relatively strong phonon scattering in Si.
- **On/off ratio.** Real FET devices are never fully "off" – there are always leakage currents (Fig. 1b). The ratio between the resistance of the "on" and "off" state determines how ideal the device is. Silicon MOSFETs have on/off ration around $10^6 - 10^{10}$.

Over the last 40 years, MOSFET-based microelectronics has made huge progress. Engineers managed to reduce the channel length, the parameter determining how compact a FET is, from a few microns in 1970s to less than 10 nanometers today. This constant improvement of technology is described by the Moore's law stating that states that "the number of transistors on a chip doubles roughly every 18 months". Now, however, Silicon is approaching the scaling limit – physical limitation of the material prevents even smaller transistors from being made. Therefore, an international research is underway for new electronic materials to supplement and replace Silicon in nanoscale ultra-efficient FETs.

1.3 Graphene and other 2D materials

In 2004, A. Geim and K. Novoselov from Manchester University used a piece of Scotch tape and a flake of graphite to controllably exfoliate a single monolayer of carbon atoms. The discovery of such monolayers, called graphene, sparked a revolution in condensed matter physics [1]. It turned out that graphene is the strongest, the most conductive, and the most flexible material ever. Graphene was found to host quasiparticles described by an effective Dirac equation (Dirac fermions) and a to possess a new degree of freedom, called pseudospin. The phenomena predicted for relativistic particles, such as Klein tunnelling, were found in graphene. In 2010, Geim and Novoselov shared a Nobel prize for "isolation of graphene" (whether they were the first to discover it, is another interesting and complex story. See Ref. 2 for one opinion about that)

More recently, other atomically-thick "two-dimensional" materials similar to graphene have been discovered. Some of these materials are semiconductors, some – insulators, some –superconductors, and some – ferromagnets. Often, "two-dimensionality" adds interesting new twists to the properties of these materials. Finally, it recently became possible to stack two-dimensional materials into more complex heterostructures with new properties. For example, it was very recently shown that two stacked layers of graphene rotated by a "magic angle" of 1.1 degrees exhibit exotic superconductivity.

1.4 Band structure and transport in graphene

Let us examine the band structure of graphene (Fig. 2c). Graphene is composed of sp^2-bonded carbon atoms in a hexagonal lattice (Fig. 2b). Carbon has four valence electrons. Of these, three electrons from covalent bonds with its neighbours, while the last p_z electron can "hop" between the neighbouring sites thereby contributing to the conductance. It is easy to calculate the band structure of graphene within the tight-binding approximation. (Interested readers should not miss all the fun, and carry out that calculation following very instructive Ref. 3). The outcome of the calculation is shown in Fig. 2c. We see that the conduction and the valence bands of graphene touch at six points (called K points) at the corners of the hexagonal Brillouin zone of graphene. As in graphene there are two atoms in the unit cell, each with one valence electron contributing to the conduction, the valence band is fully filled
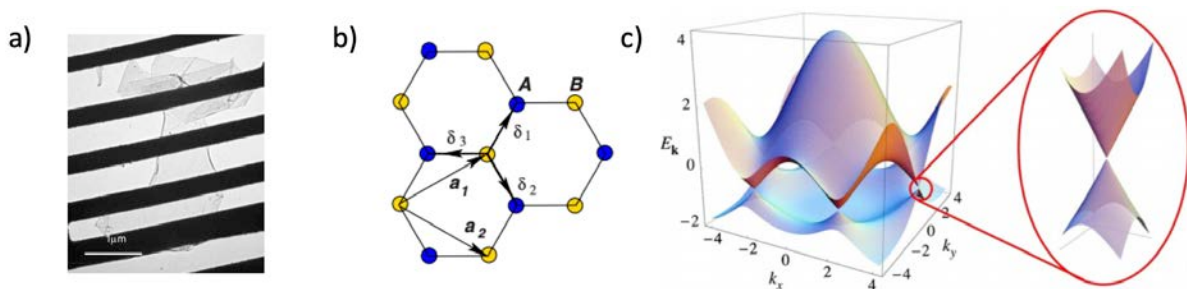
Fig. 2 a) A transmission electron microscopy image of a monolayer graphene fabricated via Scotch tape exfoliation technique, **b)** Lattice structure of graphene, **c)** Band structure of graphene obtained from tight-binding approximation calculations along with its shape near the K-points at the corners of the Brillouin zone. (Adopted from Ref. 2)

at low temperatures while the conduction band is fully empty. This means that the Fermi level is located between the conduction and valence bands.

As is shown in the courses on Condensed Matter Physics, for electronic transport only the properties of the band structure near the Fermi level matter. And now comes the critical point: near the K-points, the band structure of graphene looks like a cone in momentum space (Fig. 2c, inset). Mathematically, we have:

$$\varepsilon(k) = \pm \hbar v_F |\vec{k}| \qquad (6)$$

In this expression $\varepsilon(k)$ is the energy of electron state with momentum $K+k$ and $v_F \sim 10^6$ m/s is the Fermi velocity of graphene; electron/hole states are described by the "$\pm$". This expression is very different from the dispersion relations $(k) \sim k^2$, which we typically meet in solids. This means that the effective mass of a charge carrier is not defined in graphene. Indeed, Eq. 6 is similar to $\varepsilon(p) \sim pc$, the dispersion relation of a relativistic particle such as neutrino or photon, with v_F playing the role of the speed of light. In fact, the analogy between graphene quasiparticles and neutrinos can be taken quite a bit further: Two inequivalent "valleys" in the K-space provide a new degree of freedom for graphene electrons that behaves similar to neutrino's spin, the effective Hamiltonian describing the low-energy behaviour of carriers in graphene is formally similar to a Dirac Hamiltonian that would describe the physics of 2D neutrinos. In fact, multiple inherently relativistic phenomena that were predicted long time ago for neutrino-like particles were recently observed in a condensed matter experiments with graphene! [3]

One can already see the manifestations of the Eq. 5 in the simplest electrical transport experiment with graphene. Consider a graphene field effect transistor: an electrically contacted graphene flake deposited onto a layer of insulating silicon oxide on top of a conductive layer of silicon. Silicon serves as gate electrode (Fig. 3a, tow view in Fig. 2a). Figure 3c shows conductivity of a graphene device measured as a function of V_G applied between graphene and silicon. A large field effect is prominent in this this data! The behaviour is however very different from that of a simple Silicon transistor (Fig. 1b): conductivity first decreases with increasing V_G, and then, after about $V_G \sim$ 10V, increases again. The behaviour can be understood by examining the low-energy band structure of graphene (Fig. 2c, Inset). At large negative V_G, holes injected into graphene conduct electricity. The Fermi level is in the valence band. As V_G is increased, the hole doping is decreased and the Fermi level rises. At about $V_G \sim$ 10V, the Fermi level arrives to the middle point between the conduction and valence band ("the Dirac point") and the charge density is zero – this point is also called charge neutrality point. Is it interesting to note that the conductivity there does not turn to zero, despite zero charge density (Why do you think that is?). Finally, when V_G is further increased, the Fermi level rises into the conduction band, the electron density increases and correspondingly the conductivity grows.
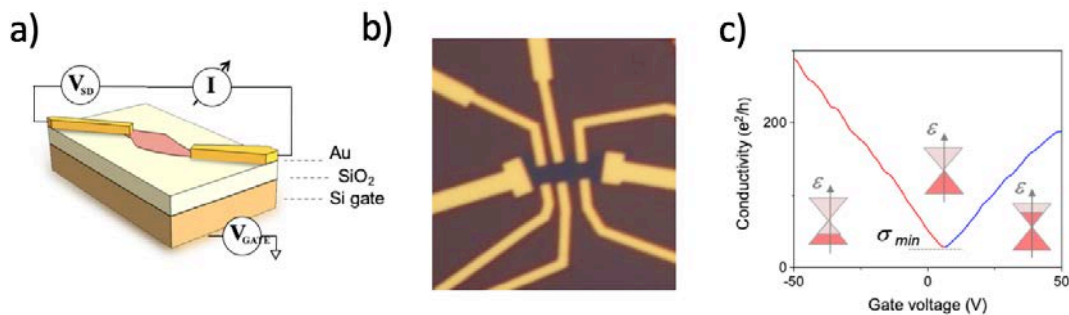
Fig. 3 a) Schematics of a graphene FET. **b)** Optical image of a fabricated device (a slightly more complex multiprobe device is shown). **c)** Conductivity vs. gate voltage for a graphene FET.

Quantitatively, the conductivity of graphene FET can be analysed using Eq. 3. While the effective carrier mass is not defined, the formula can still be applied in the form $\sigma = ne\mu$. Carrier mobility calculated for an average graphene sample on SiO_2 is about 10,000 cm^2/Vs. Surprisingly, this mobility value measured for hand-made non-pure devices in air is ten times higher than the highest mobility measured in state-of-art silicon transistors! Moreover, the resistivity of graphene in only weakly dependent on temperature. This is related to the strength of carbon-carbon bond and associated high energy of graphene optical phonons, about 120 meV. As the energy of that phonon is much larger than k_BT, few of these phonons are excited at room temperature, leading to weaker carrier scattering. It has been estimated that if disorder-related scattering in graphene is eliminated, the carrier mobility at room temperature could reach 100,000 cm^2/Vs, hundred times better than silicon [4].

At the same time, it may not be very easy to replace silicon by graphene as the lack of a bandgap in graphene leads to very small on-off ratio in graphene FETs. The emerging field of graphene electronics is attempting to resolve that problem.

2. EXPERIMENTAL

2.1 Four-probe vs. two-probe measurement

The easiest way to probe electrical transport in a device-under-test is through a two-probe measurement (Fig. 4a). The device resistance is *R = V/I*, where V is the applied voltage and I – the measured current. However, in this configuration the resistance of the wires and contacts to the devices is measured in series with the device itself. If the resistance of the device under test is comparable to the resistance of the wires, the measurement becomes inaccurate. The problem is resolved using the four-probe measurement scheme (Fig. 4b). In this approach, different terminals are used to source current and to measure the voltage drop. It is easy to see that in that geometry, the resistance *R = V/I* does not include contact or wire contribution.
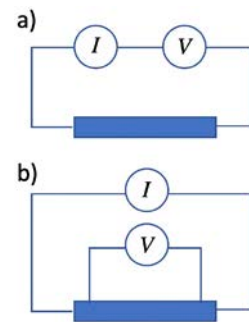
Fig. 4: Methods of the resistance measurement. a) Two-probe and **b)** four-probe.

2.2 Lock-in measurement

Various sources of noise are present in any electrical measurement. Empirically, the power spectra of many sources have *1/f* type spectra. Therefore, noise contribution can be dramatically reduced by measuring at AC rather than DC frequency. That is accomplished using the lock-in detection technique. A very good reference about the basics of lock-in detection can be found in Ref. 5.

2.3 Low temperature measurements (Cryogenics)

In order to learn about scattering mechanisms and to explore phenomena, which are hidden in the thermal noise at room temperature, it is necessary to cool the sample down. The sample is placed in a cryostat in high vacuum (P<10^{-5} mbar). Liquid nitrogen or liquid helium are used to cool the sample down to 77 K or 4.2 K respectively.
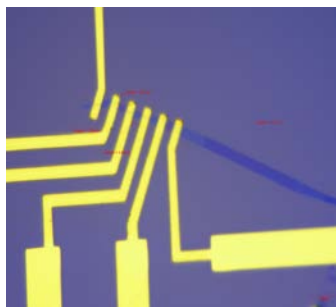
3. TASKS

List of tasks:

- Measure conductivity of graphene vs. gate voltage at room and liquid helium temperature

- Measure the conductivity of gold in two and four probe configurations at room and liquid helium temperature
- Compare measurements of conductivity using the lock-in amplifier and a DC source

We start with an introduction by the tutor to the measurement system (low-temperature probe station Fig.6). The graphene sample (Fig. 5) is mounted on the "cold finger" through which Helium or Nitrogen can flow and the chamber is evacuated to a sufficiently low pressure. After the introduction to the setup and to the measurement software (Labber), we start with some simple test measurements. This includes measuring a known reference resistance, practice on how to land a probe tip and how to determine the proper settings for the measurement devices.

Fig 5: Low-temperature probe station used for the experiment with all necessary components. The inset shows the manual motion controllers used to position the probe tips on the gold pads for contacting the sample electrically.

3.1 Measure the resistance of graphene as function of applied gate voltage at room temperature

To measure the resistance (and determine the conductivity) of graphene, we use the two-probe configuration. The first probe tip needs to be placed on the source contact and the second — on the drain contact. Additionally, the Voltage source (Keithley 2450) needs to be connected to the back gate electrode with

Fig. 6: An optical image of a graphene sample used in this lab.

a protective resistor in between. The voltage source used for the back gate allows to simultaneously record the current flowing, which shall be done at all times to check for potential electrical leakage.

First, measure the resistance of graphene device (R_{sample}) using the lock-in amplifier connected accordingly to the circuit shown in Fig. 7a. You should measure a value in the kΩ range. If so, continue by varying the gate voltage V_G and record the changes in resistance (Back gate trace). To convert resistance to conductivity, the tutor will provide the geometrical dimensions (width, length) of the device. The thickness of monolayer graphene is 0.335 nm.

The following settings of the lock-in amplifier are suggested:

- Voltage: Sets the bias voltage and depends on the resistor (typically 1 MΩ), which limits the current. For the 1 MΩ resistor, 1 V is a reasonable starting value.
- Frequency: A value between 5 and 50 Hz works best. Usually odd numbers (e.g. 18.83 Hz are used to avoid interference effects with the 50 Hz power lines).
- Phase: Adjust the phase so that the measured phase is roughly zero. This can also be done by pressing the *auto-phase* button.
- Sensitivity (range): Determines your measurement range and needs to be adjusted so that the signal equals half the sensitivity range.
- Integration time (1/bandwidth): Should be set as low as possible, but high enough to get a stable reading of the measurement value. The time/data point in the measurement software is determined by this and should be set such that the time/data point equals to 4 x integration time.
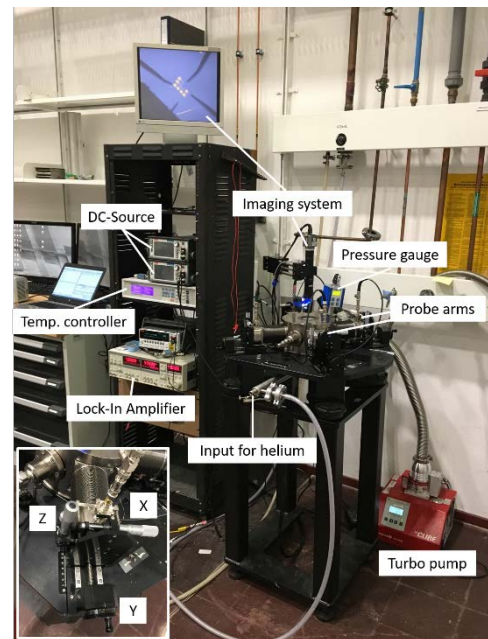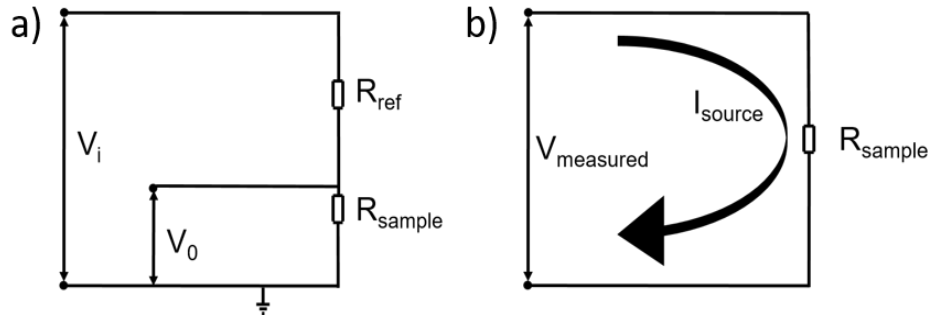
Fig 7: Electrical circuit used to measure the resistance of graphene in a two-probe configuration using a) lock-in amplifier and b) DC source. Here, R_{ref} is a known reference resistance of 1 MΩ limiting the current across graphene, V_i is the AC voltage applied by the lock-in amplifier, V_0 is the voltage drop across the sample measured by the lock-in amplifier. Finally, R_{sample} is the resistance of the graphene device under test determined as $R_{ref}V_0/V_i$.

When the back gate trace has been recorded, we switch to the DC-Voltage source (Keithley 2450) and repeat the experiment. The wiring configuration for this is shown in Fig. 7b. In this configuration, the DC source gives out a constant current and measures the voltage. From these values, one can directly calculate the sample resistance and conductivity. Record the gate voltage dependence of graphene resistance in this configuration as well.

The following settings of the DC-Source are suggested:

- *Output current* is used to set the fixed current through the sample (recommended value is 1 µA).
- *Voltage limit* is set to protect the sample
- *Integration time* is the averaging time for each data point

Compare the measurements recorded using the AC Lock-In technique and the DC Source in terms of noise and measurement time. For further experiments with graphene (e.g. Section 3.3) use only the 'better' method.
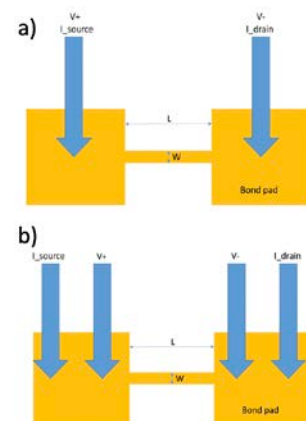
3.2 Measure the resistance of a thin gold stripe

To measure the resistance of a thin gold stripe, we use the two and four-probe configuration using the DC-Source.

At first, we use the two-probe configuration, where we place one probe on either side of the stripe on the bond pad and source a current using a DC source similar to the experiment in the Section 3.1. A sketch of the measurement configuration is shown in Fig. 8a. Record the IV characteristic of gold, sweeping the current form 0 to ±1mA.

Next, we switch to the four-probe configuration, for which an additional measurement needle is placed on each bonding pad (Fig. 8b). Again, we sweep the current from 0 to ±1mA and record the voltage. Directly compare it to the two-probe method and check if your results make sense.

Fig 8: a) Two-probe and **b)** four-probe configurations used for measuring the gold stripe.

Finally, record the dependence of the resistance of gold measured in four-probe configuration as a function of gate voltage. What do you observe?

3.3 Measure the conductivity of graphene as a function of applied gate voltage at liquid helium temperature

With the help of the tutor, liquid helium is transferred into the setup, cooling down the sample and the radiation shield. As soon as the temperature stabilizes at about 8-12K (as monitored by the temperature controller), we repeat the measurements from Section 3.1.

Please remember to withdraw the probe station needles from the sample, while changing the temperature!

3.4 Measure the resistance of a thin gold stripe at liquid helium temperature

When the system is cooled down repeat the measurement from Section 3.2.

3.5 Error considerations

Think in advance about a method on how to estimate the errors of the experiment! This should be done by an additional experiment, which shall be carried out at a given time.

4. ANALYSIS

4.1 Calculate the conductivity of graphene as a function of an applied gate voltage

Using dimensions provided by the tutor, convert the resistance measured during the experiments into geometry-independent 2D-conductivity. Plot the conductivity of the graphene sample as a function of a back gate voltage for different temperatures in one graph. Compare your data to the data in Fig. 3c. Also compare the curves obtained using the lock-in and the DC-Source techniques. Compare the noise magnitude in both measurements. Conclude, which technique do you find more preferable for the given experiment and why?

Find the charge neutrality point (V_{CNP} in Volts), the gate voltage at which the conductivity is minimal, for each temperature from the conductivity vs gate dependence. Next, calculate the areal gate capacitance C_G using the gate dielectric thickness of 295 nm and relative permittivity of SiO_2 $\varepsilon \sim 3.8$ (see Eq. 4 + 6). Please note that you are calculating the capacitance normalized per area, so the geometrical dimensions do not enter. State your value for $\alpha = C_G/e$, the so-called lever arm. Combining this information with V_{CNP}, convert the applied back gate voltage to the charge carrier density, using the Eq. 6.

$$n = \alpha \left(V_G - V_{CNP} \right) \quad (6)$$

For each temperature, plot the conductivity vs. charge carrier density and determine the carrier mobility for holes and electrons by fitting the data to $\sigma = ne\mu$. In order to get the mobility value numerically, use the highest carrier density achievable in the experiment. Furthermore, determine the ON/OFF ratio for the measured range of back gate voltages at different temperatures. Finally, calculate the Fermi energy E_F for graphene vs. V_g and try to make some estimates on the scattering times. What changes in the mobility do you see? How can you explain these changes? Do you see some weird features in your data? Any idea what that could be?

Finally determine the gate resistance from the recorded leakage current for each temperature. Is it resistive enough to not affect the operation of the graphene FET?

4.2 Measure the resistance of a thin gold stripe

For two and four-point probe determine the resistance of the gold stripe and conductivity of gold (length, width and thickness are provided by the tutor). Do the values measured using two- and four-probe methods differ? How would you explain this?

How does the resistivity value compare to the literature values for gold at room temperature (include errors here!). Also, extract the resistivity values for liquid helium temperature. Explain the observed changes with temperature. What are the mechanisms behind these changes? Explain the gate voltage dependence (or lack of thereof) for gold.

5. THINGS YOU SHOULD KNOW

- How to calculate the capacitance of a parallel plate capacitor
- How to calculate the resistance of metal stipe/rod from given dimensions, make an estimate for the resistance of a gold stripe (width 20µm, length 100µm and thickness of 90nm)
- How does the Drude formula $\sigma = ne\mu$ change for the two-dimensional case?
- When measuring the graphene device, how do you get from measured resistance to conductivity?
- How do you convert applied back gate voltage into the charge carrier density?
- How to estimate the current for $R_{ref} \gg R_{sample}$ in the lock-in configuration (Fig. 6) and thus calculate R_{sample} from the V_0 value.
- What order of magnitude of resistance to expect for a 4µm*4µm graphene stripe

6. STUDENT AND SETUP SAFETY [YOU WILL BE ASKED ON THIS!]

Overall, the sample is very sensitive to any mechanical or electrical perturbations and cryogenic liquids can potentially be dangerous. To avoid harming the students or damaging the device, you have to follow the following rules at any time:

- When handling the transfer tube and cold components, you must wear cryogenic gloves and safety goggles
- When connecting or disconnecting wires to/from the setup, you must wear a grounding wrist strap to avoid electrostatic discharge
- Electrical connections from measurement devices to the sample have to be grounded using grounding caps, unless measurements are carried out
- The sample will be electrically contacted by small metal needles/probe tips (will be demonstrated by the tutor). These needles can damage the sample, thus any vibration or mechanical motion (unnecessary touching) to the setup should be avoided. Furthermore, the needles have to be raised from the sample, whenever the temperature of the system is changed, as thermal contraction/expansion applies stress to the sample
- The voltage/current applied to the source-drain contacts and the back gate need to be carefully chosen. The bias voltage on the source-drain contacts should never exceed 100 mV (translates to current of ~ 100 µA) and the back gate voltage should be kept in the range of ±40 V
- When in doubt always ask the tutor!

7. SELF-MONITORING QUESTIONS

- What is the Drude model, carrier mobility, and scattering time?

- Which parameters vary for which material (metal, semiconductor) with temperature, applied voltage/current?
- Draw the band structure of graphene and show the position of the Fermi level for different doping.
- How does the field effect in a graphene FET work?
- What limits the mobility of graphene at room and liquid helium temperatures?
- Is the high vacuum necessary when the sample is cooled down to cryogenic temperatures? Why?
- What is the difference between the two- and four-point-measurement techniques? What technique should be used for the gold stripe? For graphene? For a semiconductor?
- What can change in the graphene sample, when applying different source-drain voltages?

8. REPORTS

When you send a report to the tutor, name it properly (group-number, experiment name, year)! Files like report.pdf will not be accepted! Please include the source files of your calculations (Origin, Matlab, Mathematica, Python, etc.) as a separate file.

9. REFERENCES

1. Neto et al., *Reviews of Modern Physics* 81 109 (2009)
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3. Online reference https://ocw.mit.edu/courses/physics/8-04-quantum-physics-i-spring-2013/study-materials/MIT8_04S13_BandGrapheneCNT.pdf
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