Engineering the electrical properties of graphene materials

Submitted by Ivan Khrapach to the University of Exeter as a thesis for
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Ivan Khrapach
December, 2012
Abstract

In this thesis the properties of graphene and its few-layers are engineered to make them highly conductive. Two different approaches were implemented to achieve this goal. One approach was to increase the concentration of charge carriers by intercalation of acceptor FeCl$_3$ molecules between graphene planes. This resulted in a highly conductive yet transparent material which can be useful for applications. Another approach was to increase the mobility of carriers by means of removing surface contamination in the current annealing process. Optimal annealing parameters were found and a reproducible cleaning method was suggested.
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Introduction

Graphene - a new 2D material

Two dimensional (2D) electronic systems have attracted enormous interest since the end of the 1970s. Aside from being present in almost every commercial semiconductor device, these systems allow access to new physical regimes such as the quantum Hall effect or weak localisation. Quantum properties specific for 2D systems find application in practical fields ranging from metrology to quantum computing.

Often 2D electronic systems are realised by exploring properties of the surfaces of bulk 3D materials (topological insulators [1]) or interfaces of two or more materials (MOSFETs, heterostructures and heterojunctions [2]). In the first case experimental study of the properties of the 2D surface is complicated by the contribution of the interior part of material. In the latter case, electrons are tightly confined to the interface, and thus occupy well defined quantized energy levels. Due to level separation being greater than the characteristic thermal excitation energy, often only the lowest energy level is occupied, and so the motion of the electrons perpendicular to the interface can be neglected. However, the electrons are free to move parallel to the interface. Therefore the considered systems are quasi two-dimensional.

Graphene (also referred to as monolayer graphene, MLG), first isolated in 2004 [3] is notable among other 2D systems. Being the first one-atom-thick material, it has charge carriers which form a genuine 2D gas. Thanks to the linear dispersion relation and chiral nature of charged quasiparticles graphene displays pseudo-relativistic phenomena, such as, for example, the Klein paradox [4] or anomalous quantum Hall effect [5]. The latter one can be observed at room temperature [6] due to the large separation of the Landau levels $E_1 = \sqrt{2e\hbar v_F^2 B}$ which is greater than the temperature smearing of the Fermi-Dirac distribution even at moderate magnetic fields. The concepts of
pseudospin and unusual Berry phase, which equals $\pi$, are also not typical for solid state physics \cite{5}. Transition from weak localisation to antilocalization in graphene, a consequence of the Berry phase $\pi$, can be realized experimentally \cite{7}. In graphene these quantum interference effects manifest themselves at high temperatures due to suppressed electron-phonon scattering. Phonon physics with such peculiarities as a negative expansion coefficient \cite{8} and the quadratic dispersion relation of flexural phonons \cite{9} does also deserve one’s attention.

Plenty of potential applications is the true locomotive of graphene research. For example, weak spin-orbit interaction makes graphene a promising material for room-temperature spintronics \cite{10}. There are examples of the use of graphene as a FET \cite{11}, although there are known problems with graphene being a zero-gap semiconductor. This causes graphene-based FETs to have a very low on-off ratio. In this regard many advances have been achieved by band-gap engineering. For example, one can develop a band gap by making narrow conductive channels (nanoribbons) \cite{12}. When talking about applications one should consider graphene as a father of the whole family of materials called few-layer graphene (FLG). For example, bilayer (BLG) and ABC-trilayer graphene (TLG) can be used for the band-gap engineering \cite{13,14} thanks to the ability to develop a band-gap in a perpendicular electric field.

Finally, charge carriers in FLGs exhibit high mobility which makes them good conductors. In conjunction with FLG’s transparency and flexibility this opens wide perspectives for optoelectronic applications of graphene and future bendable electronics \cite{15}.

Furthermore, as a real 2D material graphene is a perfect surface open to the environment. Thus graphene has a superior ability of sensing molecules \cite{16}.

Mono and few-layer graphene produced by the standard methods such as the widely used laboratory method of mechanical exfoliation of graphite to the Si/SiO$_2$ substrate \cite{3} or CVD-deposition \cite{17} provide material with characteristic mobilities up to 20000 cm$^2$/V$s$. This mobility is not high enough to access most attractive properties of graphene at low excitation energies - the main cause of the restrictions on the mobility is the scattering of the charge carriers on impurities in the SiO$_2$ dielectric layer.

There are two solutions known for improvement of graphene mobility. The first one implies etching of the dielectric layer in hydrofluoric acid (HF-etching) after which the graphene flakes become suspended and therefore free of the influence of the substrate.
Despite these flakes being contaminated and non-uniform, after current annealing procedure they demonstrate exceptionally high mobility (up to $1.5 \cdot 10^6 \text{ cm}^2/(\text{Vs})$) [19]). The main shortcomings of this method are safety issues and low survival rate of the samples after current annealing. To the best of our knowledge the mechanism of the destruction of suspended graphene at high current densities is not fully understood yet.

The other way of improving graphene transport quality is the use of a BN substrate [20]. This method provides uniform samples of high mobility (up to $0.3 \cdot 10^6 \text{ cm}^2/(\text{Vs})$) [21]). The drawbacks of this method are the sophisticated fabrication procedure, unavoidable doping of graphene and alteration of graphene's band structure by BN [22,23] and a small range of accessible carrier concentrations via electrostatic doping because of current leakage through the BN [24].

At the moment neither of these two methods can provide reproducible and scalable production of high quality graphene-based electronic devices. Thus one of the aims of this thesis is to understand the current annealing process for making it more reliable. We are also particularly interested in suspended FLG because it is recently used as a membrane for electromechanical resonators [25,26] and for strain engineering [27,28].

**Graphite intercalation compounds**

Graphite intercalation compounds (GICs) are materials which are obtained by insertion of the atomic or molecular layers of a different chemical substance (intercalant) between atomic layers of host graphite. First discovered in 1841 [29] they were an object of intensive study since 1970s [30]. GICs are possible because of layered structure of graphite - its interplanar bonds are weak and can be easily broken by intercalant molecules. In this aspect intercalation can be considered as a supereffective absorption by the whole volume of a host material. Intercalation compounds are possible with other host materials however graphite has attracted particular interest due to its high degree of structural order. Hundreds of chemical substances can serve as an intercalant for GIC [30], yielding materials with rich variety of properties.

In a GIC not every graphite interlayer gap is necessarily occupied by intercalant. In so-called stage 1 GICs, graphite and intercalant layers alternate and in stage 2 GICs, two graphite layers alternate with one intercalant layer, with the resulting superlattice unit cell extending over many atomic layers. In general, a stage index $n$ is equal to the...
number of graphite layers between adjacent intercalant layers. The level of intercalation staging determines the final properties of GICs.

The most useful property of GICs is their extremely high electrical conductivity. An order of magnitude increase in comparison to pristine graphite is achieved with many intercalants, especially strong effect is observed with AsF$_5$ [31] where a room temperature value for in-plane conductivity of corresponding compound is $\sigma_a = 6.2 \times 10^5 \Omega^{-1} \text{cm}^{-1}$. This value is comparable to that of copper $5.8 \times 10^6 \Omega^{-1} \text{cm}^{-1}$ [32]. The significant enhancement of conductivity is caused by the charge transfer between intercalant and host material layers. At the same time GICs are characterised by large anisotropy. For all compounds the c-axis conductivity $\sigma_c$ (in the direction perpendicular to the graphite) is much smaller. In case of AsF$_5$ $\sigma_a/\sigma_c = 2.7 \times 10^6$ [31]. In this thesis we are particularly interested in FeCl$_3$ intercalant, for which $\sigma_a/\sigma_c = 1.1 \times 10^4$ [33]. Although the c-axis conductivity is small it is still significant for the charge carriers to travel freely between layers, therefore the local electric potential is almost the same in two adjacent layers.

Another important property of some GICs is their intrinsic superconductivity (for example, calcium graphite CaC$_6$ with a critical temperature $T_c=11.5$K [34] and potassium graphite KC$_8$ with $T_c=0.125$K [35]).

Today GICs are most extensively used for energy storage. Intercalation of lithium ions into a graphite electrode is essentially the charging process of a standard lithium-ion battery (LIB) common in consumer electronics. Deintercalation in this case corresponds to the battery discharge. High electrical conductivity of lithium-graphite compound and capability of graphite to host large amount of lithium are the key properties of these batteries, defining their best energy density. This, together with other characteristics such as absence of memory effect and a slow loss of charge when not in use, makes LIBs one of the most popular types of rechargeable battery for portable electronics. Beyond consumer electronics, LIBs are also growing in popularity for military, electric vehicle, and aerospace applications.

Despite GICs having as high electrical conductivity as in copper, they could not be used as conductors on the commercial basis partly because of their mechanical properties and partly because of instability of most of GICs in air. Though some compounds, such as graphite-FeCl$_3$ and graphite-SbCl$_5$, are relatively stable [30]. Therefore in this thesis we explore effect of FeCl$_3$ intercalation on the conductivity and
transparency of few-layer graphene.

Modern materials to replace ITO

There is an increasing demand for touch screens, light emitting diodes, displays and photovoltaic devices [36]. All these devices have transparent conductor as a necessary element. For this purpose tin doped indium oxide (ITO) films are traditionally used. However a replacement for ITO is required as it is expensive and does not satisfy such needs of modern electronics as bendability and equal transparency at different wavelengths of light. Moreover global reserves of indium will be consumed in the nearest future [15,37]. The leading candidates to substitute ITO are carbon nanotube (CNT) networks, metallic nanostructures, graphene and hybrid materials [15,37]. To evaluate a transparent conductor one should consider its square resistance (sheet resistance) $R_s$ in conjunction with optical transmittance $T_r$ (normally at the wavelength of incident light equal 550 nm). $R_s$ is the resistance of a film which has square shape. It depends on the thickness of the film. One material is a better transparent conductor than another material if it has lower square resistance at the same transmittance (or higher transmittance at the same square resistance).

The advantage of CNT films as transparent conductors is the relative ease of fabrication: they can be obtained from a solution. This enables to adapt them to the standard roll-to-roll coating process. The best-performing CNT films have square resistance as low as $R_s = 60 \ \Omega$ when their optical transmittance is $T_r = 91\%$ [38] and $R_s = 24 \ \Omega$ when $T_r = 83.5\%$ [39]. Despite intensive work going in this direction, CNT films cannot yet perform at the desired level to demonstrate the square resistance of 10 $\Omega$ vs. transmittance of 90% [37].

Metallic nanostructures are materials of interest as well. The transparency of metallic continuous films is defined by their thickness and therefore can be easily adjusted to any desired level. Nevertheless, thin films have high square resistance (for example 300 $\Omega$ at the transparency of 80% [40]) which makes them not attractive for many applications. At the same time metallic, mostly silver meshes [41–45] can be printed on any substrate and yield better results with $R_s = 21 \ \Omega$ at $T_r = 89\%$ [42]. Furthermore, metallic grids can be produced by nanoimprint lithography [46] or roll-to roll printing [47]. The advantage of the grids is adjustable low square resistance down to 0.4 $\Omega$ at
the transmittance above 80% [47]. The application of these patterns is very limited due to the haze introduced by the light scattering on the grid and discontinuity (for the grid reported in [47] the distance between grid lines is about 300 µm). The possible solution of the latter problem is the use of a hybrid of a continuous film and a grid on top. In the work [48] 100 nm thick grid is reported to reduce the sheet resistance of a continuous 2 nm thin Ni film down to 6.5 Ω retaining high transmittance of 75%. Nevertheless the haze is still a problem to be solved.

Graphene and FLG are new promising transparent conductors. FLG has extinction coefficient (which is equal 100%−Tr) of 2.3 % per layer [49], and it can be easily scaled up to production by chemical vapour deposition (CVD) (the figures of merit are 300 Ω vs. 97.7% transmittance for the CVD-grown monolayer graphene and 40 Ω vs. 90% for the CVD-grown four-layer) [50]. One of the ways to improve these characteristics is to use graphene as a continuous film for a hybrid structure with a grid [51]. This approach gives the best to date parameters among graphene-based transparent conductors - 3 Ω vs. 90%. However the cost of additional fabrication steps increases production expences. This, together with the problem of haze, drives researchers to find other ways to enhance graphene’s conductivity.

Another way of improving the conductivity of graphene is doping. Since transmittance in this case should not depend on the sheet resistance [49], graphene with the highest doping level will perform better provided the mobility remains unchanged. Doping by AuCl₃, nitrometane [52] and nitric acid [50,52] gives sufficient effect. The best result for monolayer graphene is \( R_s =125 \, \Omega \) vs. \( Tr =97.7\% \) (corresponding concentration of charge carriers is \( 10^{13} \, \text{cm}^{-2} \)) and \( R_s =30 \, \Omega \) vs. \( Tr =90\% \) for four-layer [50]. In the case of four-layer graphene one can see that doping is inefficient for thick FLG, as the doping decreased the square resistance by just 25% of the pristine value of \( R_s =40 \, \Omega \). This is because the dopant cannot reach the internal graphene layers. The number of the adsorbed molecules depends only on the sample surface and is the same for monolayer and thicker graphene whereas the number of carbon atoms increases proportionally to the thickness. The aim to satisfy the desired sheet resistance of 10 Ω vs. 90% transmittance [37] drives us to find a more effective way to dope FLG. As it was discussed in the previous section, intercalation is a more effective way to deliver dopant molecules to the host material than adsorption.

Our attention is then focused on the donor-type FeCl₃ few-layer graphene (FLG)
intercalates where the hole density can be as high as $5.8 \cdot 10^{14}$ cm$^{-2}$ per graphene layer [30]. The FLG intercalation process has been attempted by several groups [53–55], however, without a comprehensive study of the optical and electrical properties of this novel material. Indeed, transport properties have been studied for FeCl$_3$-bilayer graphene by Kim et al. [55]. Due to the lithography element in the fabrication procedure the compound was partially deintercalated and not uniform which resulted in the low hole density of $5 \cdot 10^{13}$ cm$^{-2}$, mobility of 1200 cm$^2$/(Vs) and the square resistance of 130 $\Omega$. In all the works [53–55] transparency study was not performed as the samples were on Si/SiO$_2$ substrates.

This thesis

In this thesis we engineer the properties of graphene and FLG to enhance the electrical conductivity $\sigma$. In general, we have two ways to change the conductivity which can be seen from the equation $\sigma = n e \mu$ ($n$ is the carrier concentration, $e$ is the electron charge and $\mu$ is the carrier mobility). The first way is to increase the carrier concentration $n$ by chemical doping. We accomplish this by intercalating FeCl$_3$ molecules between graphene layers. The second way is to increase the mobility. We focus on suspended graphene and study the current annealing process to understand if it can be a reproducible method of increasing the mobility.

In Chapter 1 we present the theory background and introduction to basic properties of graphene. We begin with the discussion of the band structures of mono- and bilayer graphene. Then we address the problem of Fermi energy-dependent graphene electrical resistivity in context of Boltzmann scattering theory. Various scattering mechanisms are discussed. Thereafter we consider Shubnikov-de Haas oscillations (SdHO) and electronic transport in layered structures at low magnetic fields.

In Chapter 2 relevant techniques of sample fabrication, analysis and measurements are described. Starting with the scotch-tape technique, we consider both two-zone method of intercalation and HF-etching for suspending graphene flakes. As our study is focused particularly on FLG, we describe methods of accurate determination of the number of layers, namely, contrast and Raman analysis.

In Chapter 3 we provide the detailed study of the structure of FeCl$_3$-FLG. The Raman spectroscopy complemented by analysis of SdHO to show that FeCl$_3$ molecules
intercalate few-layer graphene, penetrating between graphene planes and decoupling them. The resulting structure corresponds to the stage I intercalation of bulk graphite. The structural analysis also reveals partial deintercalation of the outermost layer of FeCl$_3$.

In Chapter 4 we report the first study of FeCl$_3$-FLG as a transparent conductor. We show that intercalation with FeCl$_3$ does not change significantly the transparency of FLG on glass. The use FLG thicker than 3-layer allowed us to reduce sheet resistance by two orders of magnitude compared to pristine FLG (for bilayer and trilayer graphene we could not achieve such dramatic reduction). As the result, our best samples have sheet resistances as low as 15.4 Ω and 8.8 Ω with transmittances of 88% and 84% respectively, approaching the theoretical limit (11 Ω and 91%) of graphene quality suggested in literature [56, 57]. These numbers outperform parameters of ITO and other carbon-based materials [37,41], and are comparable with the parameters of the best hybrid transparent conductors known to date [51].

In Chapter 5 we experimentaly examine the electrical breakdown of suspended mono- to trilayer graphene devices. Our results reveal that the oxidation of graphene flake at the characteristic temperature of 1400 K is the cause of breakdown in most of our samples. At the same time few samples break at a temperature above 2200 K, most probably due to sublimation of carbon atoms. Our results propose a current annealing recipe optimal for reproducible significant mobility increase of suspended samples.
Chapter 1

Theoretical background

Most of the properties of graphene family materials which were used in this thesis arise from the unique electron dispersion relations of MLG and BLG. We present these spectra in the section 1.1. In order to monitor the progress of graphene quality during current annealing we measure resistance as a function of gate voltage - $R(V_G)$ characteristics. Therefore we need to understand the link between the shape of $R(V_G)$ characteristic and the transport properties such as carrier mobility and charge inhomogeneity. We devote section 1.2 to this problem. Finally, in section 1.3 we consider magnetotransport as a tool for determining the carrier density, effective mass and mobility.

1.1 Electronic structures of mono- and bilayer graphene

In monolayer graphene four valence orbitals of free carbon atom ($2s, 2p_x, 2p_y, 2p_z$) hybridise to three $\sigma$ orbitals in $sp^2$ configuration and one $\pi$ ($2p_z$) orbital. The $\sigma$ bonds cause strong coupling between carbon atoms and are responsible for graphene’s mechanical properties [58]. They do not contribute to the electron transport which is totally determined by the weak overlap between the $\pi$ orbitals. Therefore we focus on the electronic spectrum $E(\vec{k})$ of $\pi$-electrons.
In the beginning we note that graphene has two atoms (A and B) in the unit cell (Fig.1.1a). These basis atoms form two inequivalent A and B sublattices. The carbon-carbon distance is $a_0 = 1.42 \text{ Å}$. The translation vectors $\vec{a}_1$, $\vec{a}_2$ and the lattice constant $a$ are

$$
\vec{a}_1 = \frac{a}{2}(1, \sqrt{3}), \quad \vec{a}_2 = \frac{a}{2}(1, -\sqrt{3}), \quad a = \sqrt{3}a_0 = 2.46\text{Å}.
$$

The reciprocal lattice and the first Brillouin zone are shown in Fig.1.1b. The reciprocal lattice vectors are

$$
\vec{b}_1 = \frac{2\pi}{a}(1, 1/\sqrt{3}), \quad \vec{b}_2 = \frac{2\pi}{a}(1, -1/\sqrt{3}).
$$

The band structure of graphene was first derived by Wallace [59] by means of the tight-binding approach. We will briefly follow Ref. [59] to illustrate the key properties of the electron spectrum of graphene. As the graphene unit cell contains two carbon atoms, one constructs two Bloch functions $\Phi_A$ and $\Phi_B$, considering the electron wavefunction as their superposition: $\Psi = C_A\Phi_A + C_B\Phi_B$. Then one substitutes the wavefunction into the Schroedinger equation:

$$
\hat{H}|C_A\Phi_A + C_B\Phi_B\rangle = E|C_A\Phi_A + C_B\Phi_B\rangle.
$$

The resulting equation is multiplied by $\langle \Phi_A |$ and $\langle \Phi_B |$ which yields a system of linear equations for the coefficients $C_A$ and $C_B$:  

---

Figure 1.1: a) Graphene crystal lattice in the real space with the unit vectors and the unit cell (grey romb). b) Reciprocal lattice with the unit vectors and the first Brillouin zone (coloured hexagon). c) Reciprocal lattice with K and K’ valleys (blue and red triangles respectively)
\[ (C_A \langle \Phi_A | \hat{H} | \Phi_A \rangle + C_B \langle \Phi_A | \hat{H} | \Phi_B \rangle) = E(C_A \langle \Phi_A | \Phi_A \rangle + C_B \langle \Phi_A | \Phi_B \rangle) \]
\[ (C_A \langle \Phi_B | \hat{H} | \Phi_A \rangle + C_B \langle \Phi_B | \hat{H} | \Phi_B \rangle) = E(C_A \langle \Phi_B | \Phi_A \rangle + C_B \langle \Phi_B | \Phi_B \rangle) \]  
(1.1)

For simplicity one can assume that the wavefunctions centered at different atoms do not overlap (\(\langle \Phi_A | \Phi_B \rangle = \langle \Phi_B | \Phi_A \rangle = 0\)). Also, \(\langle \Phi_A | \hat{H} | \Phi_A \rangle\) and \(\langle \Phi_B | \hat{H} | \Phi_B \rangle\) represent substantially the same physical quantity: \(\langle \Phi_A | \hat{H} | \Phi_A \rangle = \langle \Phi_B | \hat{H} | \Phi_B \rangle = H_{AA}\). Finally, \(\langle \Phi_A | \hat{H} | \Phi_B \rangle = (\langle \Phi_B | \hat{H} | \Phi_A \rangle)^* = H_{AB}\) according to the properties of Hermitian operators. When all these details are taken into account the simplified system is

\[ (H_{AA} - E)C_A + H_{AB}C_B = 0 \]
\[ H_{AB}C_A + (H_{AA} - E)C_B = 0 \]  
(1.2)

with the corresponding secular equation

\[ E(\vec{q}) = H_{AA}(\vec{q}) \pm |H_{AB}|(\vec{q}). \]  
(1.3)

Here \(\vec{q}\) is the wavevector measured from the center of the first Brillouin zone (\(\Gamma\) point). To finish the tight-binding calculation one has to substitute the Bloch functions \(\Phi_A = \frac{1}{\sqrt{N}} \sum_{\vec{R}_A} e^{i \vec{q} \cdot \vec{R}_A} \varphi(\vec{r} - \vec{R}_A)\) and \(\Phi_B = \frac{1}{\sqrt{N}} \sum_{\vec{R}_B} e^{i \vec{q} \cdot \vec{R}_B} \varphi(\vec{r} - \vec{R}_B)\) into the equation (1.3). Here \(\varphi(r)\) it the normalised \(2p_z\) orbital of an isolated carbon atom. The result of such substitution in the nearest-neighbours approximation is

\[ E(\vec{q}) = \varepsilon_{2p} \pm \gamma \sqrt{1 + 4 \cos^2(q_x a/2) + 4 \cos(q_x a/2) \cos(\sqrt{3} q_y a/2)}. \]  
(1.4)

The constants in the latter equation are the matrix elements \(\varepsilon_{2p} = \langle \varphi(\vec{r} - \vec{R}_A) | \hat{H} | \varphi(\vec{r} - \vec{R}_A) \rangle\) and \(\gamma = |\langle \varphi(\vec{r} - \vec{R}_A) | \hat{H} | \varphi(\vec{r} - \vec{R}_B) \rangle| = -2.79\) eV. The dispersion relation described by the Eq. (1.4) is symmetric with respect to the energy (See Fig.1.2) \(\varepsilon_{2p}\) which is the Fermi energy of undoped graphene [58]. Therefore it is convenient to set \(\varepsilon_{2p}\) to zero.

The "+" sign in the Eq.(1.4) corresponds to the filled conduction \(\pi\) band and "-" sign - to the empty valence \(\pi^*\) band. More accurate tight-binding calculations taking into account of the finite wavefunctions overlap \(\langle \Phi_B | \Phi_A \rangle \neq 0\) and next-neighbours interaction [59] or \textit{ab initio} calculations [60] give a similar equation to Eq.(1.4), yet
with asymmetric band structure (See Fig.1.2,1.3). Nevertheless it is always symmetric in the vicinity of six K and K’ points at the corners of the Brillouin zone, where the conduction and valence bands touch each other. There is no band gap between the conduction and valence bands and thus graphene is a semimetal (or, alternatively, a zero-gap semiconductor).

![Graphene Band Structure](image1)

Figure 1.2: Nearest-neighbours tight-binding dispersion relation of MLG (green curve) in comparison with the ab initio results (red curve). Adapted from [60].

It is possible to combine three K points in one group and three K’ points in another group so that they form two continuous K and K’ valleys with the total area in k-space equal to the area of the first Brillouin zone, as shown in Fig.1.1c. The K and K’ points where conduction and valence bands touch each other are called Dirac points. The two valleys are not equivalent which comes from the inequivalence of A and B sublattices of graphene. The two valleys contribute to the electron transport independently.

![Dispersion Relation](image2)

Figure 1.3: The dispersion relation of MLG taking account of the next-neighbours interaction. The zoom-in shows a region in the vicinity of one of the Dirac points where the spectrum can be approximated as linear. Adapted from [61].
Chapter 1: Theoretical background

One can introduce a wavevector $\vec{k}$ measured from to the Dirac point: $\vec{k} = \vec{q} - \vec{K}$. In the vicinity of the Dirac point the equation for the dispersion relation Eq.(1.4) can be approximated by the linear function:

$$E(\vec{k}) = \frac{\sqrt{3}}{2} a \gamma k = h v_F k.$$  \hspace{1cm} (1.5)

Here the gradient of the linear dispersion $\sqrt{3}a\gamma/2$ is designated as $h v_F$. The charge carriers close to K and K' points have an energy-independent group velocity (Fermi velocity) $v_F \sim 10^6$ m/s. We will use this constant to describe the electronic spectrum of BLG as well. In BLG the Fermi-velocity is different from $v_F$ and depends on the energy, therefore to avoid confusion we choose the different notation $v_g F$ for the group velocity at the Fermi energy for BLG.

![Figure 1.4: Splitting of the π band in bilayer graphene.](image)

In bilayer graphene electrons have the possibility to hop between two planes of graphene. The corresponding overlap integral is equal to $\gamma_1 = 0.4$ eV [30]. The effect of such hopping is manifested in two ways [30, 62]: the splitting of π and π* bands into four subbands π₁, π₁*, π₂, and π₂* and acquisition of a finite effective mass in the vicinity of the Dirac point, as illustrated in Fig.1.4. This spectrum can be described by the hyperbolic dispersion relation at the relatively high carrier concentrations $n \lesssim 10^{13}$ cm$^{-2}$ [62]:

$$E(k) = \pm \frac{\gamma_1}{2} + \sqrt{(h v_F k)^2 + \left(\frac{\gamma_1}{2}\right)^2}. \hspace{1cm} (1.6)$$

This dispersion can be approximated as parabolic for the low carrier concentration.
(n \lesssim 3 \times 10^{12} \text{ cm}^{-2})$ [63]:

$$E(k) = \pm \frac{(v_F \hbar k)^2}{\gamma_1},$$

(1.7)

with effective mass $m^* = \gamma_1/2v_F^2 = 0.032m_e$. BLG is a zero-gap semiconductor with massive charged particles near K and K’ points, where $\pi_1$ and $\pi_1^*$ subbands touch each other.

At high carrier concentrations both MLG and BLG spectra have trigonal warping due to three-fold symmetry of the K and K’ valleys. The warping breaks $\vec{p} \rightarrow -\vec{p}$ symmetry of the dispersions (1.5) and (1.6). The effect is much stronger in bilayer graphene [64]. For example in quantum effects like weak localisation, where dephasing destroys the interference, the trigonal warping completely suppresses localisation in disorder-free samples [64, 65]. At the same time this does not seem to affect the quantum Hall effect and Shubnikov-de Haas oscillations up to the carrier concentrations $n \sim 3 \times 10^{13} \text{ cm}^{-2}$ [62, 66].

Both MLG and BLG have identical dependence of the carrier concentration $n$ on the Fermi wavevector $k_F$ for degenerate electron gas ($k_B T \ll E_F$) (provided that we consider only $\pi$, $\pi^*$ in MLG and $\pi_1$, $\pi_1^*$ in BLG, which practically means that $E_F < 3$ eV for MLG [58] and $E_F < 0.4$ eV for BLG [30]). In order to find it let us consider a rectangular sample with the dimensions $L$ and $W$. From the periodic boundary conditions one can determine the allowed wavevector values as

$$\vec{k} = 2\pi \left(\frac{i}{L}, \frac{j}{W}\right),$$

with $i$ and $j$ being integer numbers. Then one can obtain the number of states with energies less than $E_F$ by dividing the area of the circle of radius $k_F$ by the area in $k$-space of one state, $\Delta k_x \Delta k_y = 4\pi^2/(LW)$:

$$N = g \frac{\pi k_F^2}{\Delta k_x \Delta k_y} = \frac{gLWk_F^2}{4\pi},$$

(1.8)

where $g$ is the degeneracy of one $k$-state. In MLG and BLG, in addition to the spin degeneracy $g_s = 2$ there is also a valley degeneracy $g_v = 2$, such that, $g = 4$. Taking this into account the carrier concentration is
Chapter 1: Theoretical background

\[ n = N/LW = k_F^2/\pi. \] (1.9)

Likewise, using Eq.(1.8) we can obtain the number of states within the range of wavevectors \( (k, k + dk) \) by dividing the area within this range of wavevectors \( 2\pi k dk \) by the area of one state, \( \Delta k_x \Delta k_y = 4\pi^2/(LW) \):

\[ dN = 4\frac{LWkdk}{2\pi}. \]

This is helpful to find the density of states:

\[ D(E) = \frac{1}{LW} \frac{dN}{dE} = \frac{g}{2\pi} \frac{dk}{dE} = \frac{2k}{\pi} \frac{dk}{dE}. \] (1.10)

Substituting the linear dispersion relation from (1.5) we obtain

\[ D(E) = 2\frac{E}{\pi \hbar^2 v_F^2}. \] (1.11)

The density of states for BLG at relatively low energies (when we can use the parabola approximation for the dispersion relation) does not depend on the energy and can be obtained by substituting Eq.(1.7) into Eq.(1.10):

\[ D(E) = 2m^*/\pi \hbar^2. \] (1.12)

1.2 Electrical conductivity of mono- and bilayer graphene and scattering mechanisms

Within the scope of this work we will deal with the electric transport in MLG and FLG in weak magnetic fields at Fermi energies far from the Dirac point \( (E_F \text{ ranging from } 3 \text{ meV to } 1 \text{ eV}) \). In this energy range the semiclassical approach have been used to describe the density- and temperature dependent resistivity of MLG and FLG [61]. This section presents a quick review of this topic.
1.2.1 Semiclassical theory of electrical conduction

Except for a limited range of energies near the Dirac point one operates with the doped MLG or FLG, when the electron gas is degenerate. This is most prominent in MLG where, according to Eq.(1.5) and Eq.(1.9) $E_F = \hbar v_F \sqrt{\pi n}$ and the Fermi energy is greater than $k_B T$ already at the carrier concentration $n \sim 10^{10}$ cm$^{-2}$. Therefore in order to address the problem of electrical conductivity of BLG and MLG we first consider the finite charge density. High $n$ also means a large number of electrons below the Fermi level (or holes above the Fermi level). Then the semiclassical approach can be used and the current density is a sum over current contributions given by all occupied states:

$$\vec{j} = \int e \vec{v}_g \varphi \, d\varphi = \int e \vec{v}_g f_0(\vec{k}) g \frac{d\vec{k}}{4\pi^2} + \int e \vec{v}_g f_1(\vec{k}) g \frac{d\vec{k}}{4\pi^2}, \quad (1.13)$$

where $f_0$ is the probability density function in equilibrium (described by the Fermi-Dirac distribution) and $f_1$ is the perturbation of the probability density. In the relaxation-time approximation and in the limit of weak electric field $\vec{E}$ the latter one can be written as [67]:

$$f_1 = -\tau_e \frac{\partial f_0}{\partial E} \vec{E} \cdot \vec{v_g}. \quad (1.14)$$

Substitution of Eq.(1.14) into (1.13) results in the general formula for the electrical conductivity of a 2DEG:

$$\sigma = -\frac{e^2}{2} \int \tau v_g^2 D(E) \frac{\partial f_0}{\partial E} dE. \quad (1.15)$$

From this equation we can immediately obtain the conductivity of a 2D degenerate gas (assuming $df_0/dE = -\delta(E)$):

$$\sigma = \frac{e^2}{2} D(E_F) v_g^2 \tau(E_F). \quad (1.15)$$

It is convenient to express the density of states in the Eq.(1.15) via carrier concentration, $D(E) = dn/dE = \frac{dn}{dk} \frac{dk}{dE} = 2\pi \frac{1}{k v_g \hbar}$. Then the conductivity is equal to

31
\[ \sigma = n e \left( \frac{e v_F}{\hbar k_F} \tau(E_F) \right). \] (1.16)

Using this formula one can get the general formula for the mobility \( \mu = \sigma / ne \) of a degenerate 2DEG as

\[ \mu = \frac{e v_F}{\hbar k_F} \tau(E_F). \] (1.17)

To proceed with the application of these expressions to the particular cases of MLG and BLG one has to determine the scattering time. The next subsection is devoted to this problem.

### 1.2.2 Scattering mechanisms

Among the numerous scattering mechanisms limiting the conductivity of graphene and its multilayers the three most important ones are the following \[68\]: scattering off charged impurities (long-range scattering, \( \tau_{LR} \)) \[69\], scattering off sharp neutral contaminants and structural defects (short-range scattering, \( \tau_{SR} \)) \[70\] and electron-phonon interaction (\( \tau_{ph} \)) \[9,71,72\]. The first mechanism is dominant for the supported samples due to significant amount of impurities in SiO\(_2\) \[18\]. In clean suspended samples or at elevated carrier densities in MLG the other two mechanisms can become more important \[72\]. The summary of the scattering times and conductivities (case of degenerate gas, Eq.(1.16) corresponding to these mechanisms is given in the Table 1.1

<table>
<thead>
<tr>
<th>Scattering mechanism</th>
<th>Scattering time MLG</th>
<th>Conductivity MLG</th>
<th>Scattering time BLG</th>
<th>Conductivity BLG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Long-range</td>
<td>( \tau_{LR} = \frac{k}{\pi^2 v_F^2 n_i v} )</td>
<td>( \sigma_{LR} = \frac{2e^2}{h} \frac{n}{n_i} )</td>
<td>( \tau_{LR} = \frac{2m^*}{C^2 \pi \hbar n_i} )</td>
<td>( \sigma_{LR} = \frac{2ne^2}{C^2 \pi \hbar n_i} )</td>
</tr>
<tr>
<td>Short-range</td>
<td>( \tau_{SR} = \frac{4h^2 v_F}{n_d V_0^2 k} )</td>
<td>( \sigma_{SR} = \frac{4e^2 h v_F}{n_d V_0^2 \pi} )</td>
<td>( \tau_{SR} = \frac{h^3}{n_d V_0^2 m^*} )</td>
<td>( \sigma_{SR} = \frac{ne^2 h^3}{(m^*)^2 n_d V_0^2} )</td>
</tr>
<tr>
<td>Phonons</td>
<td>( \tau_a = \frac{2\rho_s h^3 v_F c^2}{D_\gamma^2 k F k_B T} )</td>
<td>( \sigma_a = \frac{2e^2 \rho_s h v_F c^2}{\pi D_\gamma^2 k_B T} )</td>
<td>( \tau_a = \frac{4\rho_s h^3 v_F c^2}{D_\gamma^2 \gamma_1 k_B T} )</td>
<td>( \sigma_a = \frac{ne^2 4\rho_s h^3 v_F c^2}{m^* D_\gamma^2 \gamma_1 k_B T} )</td>
</tr>
</tbody>
</table>

Table 1.1: The most important scattering mechanisms in MLG and BLG

In this table \( r_s = 0.8, C \approx 2.03 \) are constants, \( n_i \) is the concentration of charged impurities, \( n_d \) is the concentration of defects and neutral contaminants, \( V_0 \) is the strength of the defect scattering potential, \( \rho_s \) is the 2D mass density of graphene, \( c \) is the
speed of sound in graphene and $D_a$ is acoustic deformation potential. Some other scattering mechanisms were proposed in literature, such as resonant scatterers [70,73] or ripples [74], however their influence is disputable since it is sample-dependent and hard to distinguish experimentally from the mechanism listed in Tab1.1. Therefore they are not accounted in this work. We consider only acoustic phonons, although flexural phonons [9,68,72] and substrate phonons [75] can also give a significant contribution depending on the sample fabrication technique. It is important to notice that surprisingly in supported BLG the phonon contribution have not been detected yet [20,68]. Therefore in BLG there are only two major sources of scattering which are temperature-independent and have the same dependence on the carrier concentration. This results in the total conductivity linearly dependent on the carrier concentration with the constant mobility $\mu = e(\frac{2}{C_2\pi h^2} + \frac{h^3}{(m^*)^2 n d V_0})$:

$$\sigma_{BLG} = n e \mu$$

$$\rho = \frac{1}{n e \mu}.$$  \hspace{1cm} (1.18)

According to the Matthiessen’s rule the total conductivity in MLG is given by

$$\sigma_{MLG}^{-1} = \sigma_{LR}^{-1} + \sigma_{SR}^{-1} + \sigma_{ph}^{-1}.$$  

This leads to the resistivity being a sum of a T-independent, n-dependent term due to long-range scattering and a n-independent, T-dependent term due to phonons and short-range scattering:

$$\rho_{MLG} = \frac{1}{n e \mu_{LR}} + \rho_{SR}(1 + AT)$$  \hspace{1cm} (1.19)

1.2.3 Typical $R(V_G)$ dependencies

The dependencies of MLG and BLG resistivities on the carrier concentration Eqn.(1.19) and (1.18) manifest themselves in the $\rho(V_G)$ characteristics (See Fig.1.5). One can control carrier concentration of graphene-based transistor via electrostatic doping. Usually the doping is proportional to gate voltage $V_G$ (See chapter 2 for details) and therefore the functional dependence $\rho(V_G)$ resembles that of $\rho(n)$. One can see a sharp peak close to the neutrality point $V_G = 0$ which corresponds to the position of the Fermi level at the Dirac point, $n = 0$. At the same time, the corresponding $\sigma(V_G)$ characteristics has a
V-shape in agreement with Eq.(1.19). Moreover, one can deduce a density-independent resistivity $\rho - \text{const} = \rho_L$ for MLG to obtain an exactly linear $\sigma_L(V_G) = 1/\rho_L$ [68]. This supports existence of both long-range and short-range scatterers in MLG.

![Figure 1.5: Resistivity (blue curve) and conductivity (green curve) of MLG as a function of gate voltage. The red curve on the plot represents the conductivity due to long-range scattering $1/(\rho - \text{const})$, where const is the contribution due to short-range scattering. Adapted from [68].](image)

The resistance at the neutrality point at low temperatures does not diverge mostly because of the electron-hole puddles [69,76]. Puddles are the regions of slightly varying doping which shifts the position of Dirac point randomly. Therefore The Fermi level is never placed exactly at zero energy all over the sample. As a consequence the carrier concentration in Eq.(1.18) and (1.19) is never less than a certain limit $n^*$ which defines the maximum resistivity. $n^*$ depends on the nature and amount of contamination and is of the order of $\sim 10^{11}$ cm$^{-2}$ [56]. This corresponds to the depth of puddles in the energy scale $\Delta E = \hbar v_F \sqrt{\pi n^*} \sim 50$ meV $\sim 2k_B T$ for MLG at room temperature. Therefore even at the gate voltages close to neutrality point charge carriers behave as degenerate ones and the only source of temperature dependence is the phonon contribution to the resistivity.

The depth of puddles for BLG is $\Delta E = n^*/D(E) \sim 7$ meV $< k_B T$. At the temperatures above 10÷60 K (depending on the purity of the sample) charge carriers in BLG
can not be described as degenerate in the vicinity of the neutrality point and the resistance drops dramatically (Fig.1.6a). At higher temperatures the thermal excitation affects resistance at increasingly higher gate voltage, in accordance with $n_T \sim D(E)k_B T$.

![Figure 1.6: Temperature- and density dependent resistivity of bilayer graphene (a) and trilayer graphene (b).]

The temperature- and density dependent charge transport in both ABA and ABC trilayer graphene (TLG) is the problem which has not been studied in details to date. Nevertheless the $R(V_G)$ characteristics and the temperature-dependence $R(T)$ are similar to those of bilayer graphene (Fig.1.6b). This is the manifestation of the electronic spectrum of ABA-TLG which is the combination of MLG and BLG spectra at low energies [77, 78]. Since the density of states of MLG is vanishing at the Dirac point (Eq.(1.11)) while that of BLG stays finite (Eq.(1.12)) the electron transport in TLG is dominated by the states with parabolic dispersion.

To conclude, the $R(V_G)$ characteristics of MLG, BLG and TLG have similar peak shape at low temperatures when one can neglect the thermal excitation. This shape is described by the mobility which weakly depends on carrier concentration. The higher the mobility is the sharper and narrower is the peak at the neutrality point. In Chapter 5 we use $R(V_G)$ measured at low temperature to characterise MLG, BLG and TLG samples before and after current annealing.
1.3 2D electron (hole) gases in weak magnetic field.

1.3.1 Shubnikov-de Haas oscillations

As it was shown in the subsection 1.2.1 the semiclassical approach can adequately describe the properties of graphene and its bilayer at high enough carrier concentrations. Let us apply this approach to electron dynamics in magnetic field. First, we will find the cyclotron masses for the linear spectrum of MLG and for the hyperbolic approximation of the spectrum of BLG. To do so one needs to consider the collisionless equation of motion of an electron wavepacket in k-space in a magnetic field:

\[
\hbar \frac{d\mathbf{k}}{dt} = -e \mathbf{v}_g \times \mathbf{B},
\]

where \(v_g\) is the electron group velocity on the Fermi surface. Let us neglect the trigonal warping and assume that the intersection of the electron dispersion relation \(E = E(k)\) and the constant-energy surface \(E = \text{const}\) is a circle. Then magnetic field causes rotation of the wavevector around K point with a frequency \(\omega_c\):

\[
\frac{d\mathbf{k}}{dt} = \omega_c \times \mathbf{k}.
\]

Substituting (1.21) into (1.20) gives

\[
\omega_c = \frac{ev_g}{\hbar k_F} B.
\]

Now, comparing the expression (1.22) with that of free electron \(\omega_{\text{free}} = eB/m\) one can define the cyclotron mass as

\[
m_c = eB/\omega_c = \hbar k_F / v_g.
\]

This formula is in agreement with the general expression \(m_c = \frac{\hbar^2}{2\pi} \frac{dS}{dE}\) [67] provided the area covered by the cyclotron orbit in k-space \(S\) is symmetric. Application of the Eq.(1.23) to MLG (1.5) yields energy-dependent cyclotron mass

\[
m_c = E_F / v_F^2 = \hbar \sqrt{\pi n} / v_F.
\]
In order to apply Eq.(1.23) for BLG we use the hyperbolic dispersion relation Eq.(1.6) to find the group velocity
\[
v_g = \frac{dE}{(\sim dk)} = \frac{\sim kv_F^2}{\sqrt{(hv_Fk_F)^2 + (\gamma/2)^2}} \]
which results in the cyclotron mass
\[
m_c = \frac{\sqrt{(hv_Fk_F)^2 + (\gamma/2)^2}}{v_F^2} = \frac{\sqrt{(hv_F)^2\pi n + (\gamma/2)^2}}{v_F^2}. \tag{1.25}\]

Now we can find the energy quantisation in the magnetic field. Making a start from the Bohr-Sommerfeld condition
\[
H = \int \vec{p} \cdot d\vec{r} = (N + \gamma)^2 \pi \sim, \]
one can show for any dispersion relation that electron orbits are quantised in such a way that the magnetic flux through them is equal \[67]\n\[
\Phi_N = BA_N = (N + \gamma)\frac{2\pi\hbar}{e}. \tag{1.26}\]

Here \(\gamma = 1/2 + \)Berry phase \[79]. It is more convenient to consider cyclotron orbits in \(k\)-space. To do so we convert the orbit area in real space \(A_n\) to the area in \(k\)-space using Eq.(1.20):
\[
\hbar \frac{d\vec{k}}{dt} = -e \vec{d}\tau \times \vec{B},
\]
\[
\frac{d\vec{k}}{dk} = -\frac{e}{\hbar} \vec{d}\tau \times \vec{B},
\]
\[
\vec{k} = -\frac{e}{\hbar} \vec{\tau} \times \vec{B},
\]
and therefore
\[
S_N = \frac{1}{2} \int \vec{k} \times d\vec{k} = \frac{e^2}{2\hbar^2} \int (\vec{\tau} \times \vec{k}) \times (d\vec{\tau} \times \vec{B}) = \frac{e^2}{\hbar^2} \vec{B}(B \frac{1}{2} \int \vec{\tau} \times d\vec{\tau}), \tag{1.27}\]
thus
\[
S_N = \left(\frac{eB}{h}\right)^2 A_N \tag{1.28}\]
Finally, the quantisation condition is
\[
S_N = (N + \gamma)\frac{2\pi e}{h} B. \tag{1.29}\]
Chapter 1: Theoretical background

It is valid for any electron spectrum as it operates with the orbit area in k-space
\[ S_N = \pi k_F^2 = \pi^2 n. \]
At large quantum numbers \( N \gg 1 \) and fixed carrier concentration the Fermi level crosses a maximum of the density of states when the magnetic field satisfies the condition Eq.(1.29). According to Eq.(1.15) this causes maxima in the conductivity which are known as Shubnikov-de Haas oscillations (SdHO). The conditions for two successive maxima are:

\[
\pi^2 n = (N + \gamma) \frac{2\pi e}{h} B_N, \quad \text{and} \quad \pi^2 n = (N + 1 + \gamma) \frac{2\pi e}{h} B_{N+1},
\]

thus

\[
\pi^2 n \left( \frac{1}{B_{N+1}} - \frac{1}{B_N} \right) = \frac{2\pi e}{h}. \quad (1.30)
\]

As one can see, the maxima of the resistivity are equally spaced if one considers the conductivity as a function of inverse magnetic field: \( \sigma(1/B) \). The relation between the frequency of SdHO \( f_{SdHO} = \frac{1}{1/B_{N+1} - 1/B_N} \) and the carrier concentration is clear from (1.30) and does not depend on the carrier spectrum:

\[
n = \frac{4e}{h} f_{SdHO}. \quad (1.31)
\]

It is interesting that one can obtain the exact structure of energy levels for MLG in magnetic field (Landau levels) using Eq.(1.29) despite the Bohr-Sommerfeld condition is valid only for \( N \gg 1 \). Indeed, for electrons in MLG \( S_N = \pi k_F^2 = \pi E_N^2 / (\hbar v_F)^2 \), and therefore

\[
E_N^2 = 2e\hbar v_F^2 B(N + \gamma).
\]

It is known that due to the Berry phase of Dirac-like electrons being equal to \( \pi \), the phase coefficient \( \gamma = 0 \) [79]. Then

\[
E_N = \sqrt{2e\hbar v_F^2 BN}.
\]
Landau levels with such energies are not equally separated and are in agreement with the density-dependent cyclotron frequency in Eq.(1.22).

One can observe SdH oscillations if the disorder smearing of the Landau levels is less
than the cyclotron energy $\hbar/\tau < \hbar \omega_c$ or, in other words $1 < \mu B$. The latter formula is useful to estimate the so-called quantum mobility $\mu = 1/B_s$ if the onset of oscillations $B_s$ is known. This mobility is close to the Hall or field-effect mobility. More precisely, the onset of SdHO together with their temperature decay is described by the equation [80]:

$$\Delta \sigma_{xx} \propto \frac{\frac{2\pi^2 k_B T_m c}{\hbar B}}{\sinh \left( \frac{2\pi^2 k_B T_m c}{\hbar B} \right)} \exp \left( -\frac{\pi}{\mu B} \cos \left( 2\pi \frac{n}{4e} \frac{1}{B} \right) \right).$$

(1.32)

This equation is valid for both parabolic and linear spectra [79, 81]. The valley degeneracy is taken into account. One can see that if the magnetic field is fixed the amplitude of SdHO oscillations decays according to the following law:

$$\frac{A(T)}{A(0)} \propto \frac{\frac{2\pi^2 k_B T_m c}{\hbar B}}{\sinh \left( \frac{2\pi^2 k_B T_m c}{\hbar B} \right)}$$

(1.33)

The equations (1.31) and (1.33) will be used in the Chapter 3 for determining the concentration and cyclotron mass of the charge carriers in FeCl$_3$-FLG from the frequency and the rate of the decay of SdHO with temperature.

1.3.2 Parallel conduction in weak magnetic fields

As we have seen in the subsection 1.2.1 analysis based on the Boltzman equation results in the Drude formula for the electrical conductivity of a degenerate 2DEG for both linear and parabolic dispersion relations. Therefore, according to the Drude model, electric field and the current density in weak magnetic field perpendicular to a 2DEG are related via the conductivity matrix

$$\vec{j} = \frac{\sigma_0}{1 + (\mu B)^2} \begin{pmatrix} 1 & \mu B \\ -\mu B & 1 \end{pmatrix} \begin{pmatrix} E_x \\ E_y \end{pmatrix}, \quad \vec{E} = \frac{1}{\sigma_0} \begin{pmatrix} 1 & -B/ne \\ B/ne & 1 \end{pmatrix} \begin{pmatrix} j_x \\ j_y \end{pmatrix}.$$  (1.34)

The latter formula is useful when the direction of the electric current is known to be parallel to the edge channel (along $x$ axis). In this case a transverse component of the electric field arises, resulting in the Hall voltage

$$V_{xy} = E_y W = \frac{j_x B W}{n e} = \frac{IB}{n e}.$$  (1.35)
By measuring $V_{xy}$ one can define the Hall carrier concentration $n_H = -IB/V_{xy}e$ which is equal to the carrier concentration of a single 2DEG.

Now we apply the same approach for two coexisting parallel gases. This case is different from that of two separated parallel conductors, where due to different carrier concentrations the value of the Hall voltage can be different. In contrast, two coexisting parallel gases feel the same electric field which makes the Hall voltage being equal for both of them.

In this case the current density vector of each gas may not be parallel to the channel edge for each electron gas. Nevertheless the total current

$$j = j_1 + j_2 = \begin{vmatrix}
\frac{\sigma_{01}}{1+(\mu_1 B)^2} + \frac{\sigma_{02}}{1+(\mu_2 B)^2} & \frac{\sigma_{01}\mu_1 B}{1+(\mu_1 B)^2} + \frac{\sigma_{02}\mu_2 B}{1+(\mu_2 B)^2} \\
-\frac{\sigma_{01}\mu_1 B}{1+(\mu_1 B)^2} - \frac{\sigma_{02}\mu_2 B}{1+(\mu_2 B)^2} & \frac{\sigma_{01}}{1+(\mu_1 B)^2} + \frac{\sigma_{02}}{1+(\mu_2 B)^2}
\end{vmatrix} \begin{pmatrix} E_x \\ E_y \end{pmatrix}$$

(1.36)

is parallel to $x$ according to the charge conservation law. In order to find the Hall voltage we have to invert the conductivity matrix and obtain the resistivity matrix. Neglecting the terms of third and higher order in magnetic field the resulting matrix is:

$$\rho = \begin{pmatrix}
\frac{(\sigma_{01}+\sigma_{02})^2+\sigma_{01}\sigma_{02}(\mu_1-\mu_2)^2B^2}{(\sigma_{01}+\sigma_{02})^3} & -\frac{B q_1 n_1 \mu_1^2 + q_2 n_2 \mu_2^2}{(\sigma_{01}+\sigma_{02})^3}
\\
\frac{B q_1 n_1 \mu_1^2 + q_2 n_2 \mu_2^2}{(\sigma_{01}+\sigma_{02})^3} & \frac{(\sigma_{01}+\sigma_{02})^2+\sigma_{01}\sigma_{02}(\mu_1-\mu_2)^2B^2}{(\sigma_{01}+\sigma_{02})^3}
\end{pmatrix}.$$  

Here $q_{1,2} = e$ for holes and $-e$ for the electrons. The Hall voltage is

$$V_H = \frac{IB}{e} \frac{(q_1 n_1 \mu_1^2 + q_2 n_2 \mu_2^2)}{(\sigma_{01}+\sigma_{02})^2}$$  

(1.37)

and therefore the Hall carrier concentration depends not only on the densities of each parallel gas but also on their mobilities. For the case of two hole gases the Hall carrier concentration, according to Eq.(1.37), is $n_H = (n_1 \mu_1 + n_2 \mu_2)/(n_1 \mu_1^2 + n_2 \mu_2^2)$. The generalisation of this equation for more than two hole gases is

$$n_H = \frac{(\sum n_i \mu_i)^2}{\sum n_i \mu_i^2}.$$  

(1.38)

This equation will be used in Chapter 3. Another remarkable property of the coexisting parallel gases described by the Drude model in weak magnetic field is their parabolic magnetoresistance, which can be found from the diagonal element of the
resistance matrix:

\[
\frac{\Delta \rho_{xx}}{\rho_{xx}} = \frac{\sigma_0 \sigma_0 (\mu_1 - \mu_2)^2}{(\sigma_0 + \sigma_0)^2} B^2.
\]  

(1.39)
Chapter 2

Sample fabrication and analysis techniques

In this chapter we describe the methods of sample fabrication and analysis applied in this work. We produce all our samples starting with the mechanical exfoliation followed by the electron beam lithography (EBL) and wet etching for making suspended devices, or by FeCl$_3$-intercalation and EBL for fabricating FeCl$_3$-FLG. Our study is focused particularly on FLG therefore we describe methods of accurate determination of the number of layers $N_L$. After the MLG or FLG flakes are exfoliated we determine $N_L$ from optical contrast of the flakes in comparison to the substrate and then confirm the obtained number by Raman analysis. At the end of the chapter the relevant measurement techniques are briefly discussed.

2.1 Sample fabrication

2.1.1 Supported graphene

Graphene flakes for this work were obtained by mechanical cleavage (the so-called scotch tape technique) [3]. In this method one begins with graphite of high quality with large polycrystals as shown in Fig. 2.1a. We use natural graphite (Graphenium, NGS Naturgraphit GmbH). In order to obtain graphene flakes one puts a crystal of bulk graphite to a sticky tape as shown in Fig. 2.1b. Then the tape is stuck and peeled off several times until it is covered with thin semitransparent flakes (Fig. 2.1c). At the next step the tape is put in contact with a substrate and pressed (Fig. 2.1d). After the
Chapter 2: Sample fabrication and analysis techniques

Figure 2.1: Mechanical exfoliation of graphite. a) Optical microphotograph ($\times 5$ objective) of natural graphite - a starting material with large monocrystals and of high intrinsic quality. b) Exfoliation process involving a sticky tape. c) A tape with the semi-transparent thin graphitic flakes. d) Transfer of graphitic flakes to a substrate.

We use Si/SiO$_2$ and glass substrates. The Si/Si$_2$ substrate consists of two layers: the heavily doped Si which is used as a gate and the top 285 nm thick layer of thermally oxidised SiO$_2$, which serves as a gate dielectric (Fig. 2.2a). We use the standard 100 $\mu$m thick microscope cover slips as glass substrates because they are known for the low surface roughness.

In order to put metallic contacts onto a selected FLG flake for the transport measurements we perform electron-beam lithography. At first we cover the substrate with two layers of polymethylmethacrylate (PMMA) which serves as a positive electron resist Fig. 2.2a. PMMA of the bottom layer is softer than the one of the top layer as
Figure 2.2: The key steps of E-beam lithography. a) A substrate is covered with two layers of PMMA of different molecular mass (the harder PMMA is on top). This is followed by exposure of selected regions of PMMA to the electron beam. b) The exposed regions of PMMA are washed away in a developer. Due to softness of the bottom layer of PMMA the structure has an undercut profile. c) Cr/Au contacts are evaporated. d) The unnecessary PMMA regions are washed away in the lift-off process in acetone. e) If necessary the resulting structure is placed in the buffered oxide etch to remove Si/SiO$_2$ underneath the flake.

it has a lower molecular mass. Secondly the pattern of the contacts is exposed by the electron beam. At the next step the pattern is developed in methyl ethyl ketone/methyl isobutyl ketone/isopropanol mixture which opens the regions where the contacts are intended to be present, while the rest of the substrate is still covered with PMMA (Fig. 2.2b). Soft PMMA is more soluble in the developer and therefore this leads to an undercut profile which prevents an overlap between metal layers evaporated on the structure at the next step (Fig. 2.2c). We use Au contacts because gold is a good and chemically stable conductor of electricity. A thin layer of Cr deposited before Au provides a better adhesion to graphene and the substrate. The thicknesses of the metal films are typically 10-20 nm and 100nm for Cr and Au, respectively. The large size and thickness of the electrodes enhances the mechanical rigidity of the device. At the final step we place the substrate in acetone to remove the PMMA together with the metallic film on top of it (lift-off), as shown in Fig. 2.2d. The substrate with the resulting structure can then be etched in the HF acid for suspension of the FLG membrane (see Fig. 2.2e and subsection 2.1.2) or mounted inside a chip carrier straight away for electrical characterisation.
2.1.2 HF etching

For making a suspended graphene device we start with a graphene transistor fabricated on a Si/SiO\(_2\) substrate as described above. We dip the entire device into the buffered oxide etch (BOE, a volume ratio 6:1 solution of 40% NH\(_4\)F in water to 49% HF in water) for 60 s, which uniformly removes approximately 100 nm of SiO\(_2\) across the substrate. SiO\(_2\) covered by the gold contacts remains unetched. The area below the flake is uniformly etched at a much faster rate irrespective of the lateral size of the flake which is crucial for the fabrication process because this results in the large-area suspended graphene, with the plain capacitor geometry for our device. Etching catalysis in the presence of graphene is due to rapid propagation of BOE along the SiO\(_2\)/graphene interface [18].

To stop the etching process the substrate is transferred from BOE to water and after that to pure isopropanol. The latter one is warmed up to 50°C. The heating reduces significantly the surface tension of this liquid and makes it possible to dry the substrate in atmosphere without collapse of graphene membranes because of capillary forces [14]. An example of a scanning electron microscope (SEM) micrograph of a typical suspended graphene device is shown in Fig. 2.3.

![Figure 2.3: An SEM microphotograph of a typical suspended FLG device.](image)

2.1.3 Two-zone intercalation method

We perform intercalation of FeCl\(_3\) molecules into FLG flakes deposited on glass before the electron-beam lithography. Following [30] we utilise the two-zone method. The intercalation process is performed in vacuum. Anhydrous FeCl\(_3\) powder and the substrate with exfoliated FLG are positioned in different zones inside a glass tube.
The tube is pumped down to $2 \times 10^{-4}$ mbar at room temperature for 1 hour to reduce the contamination by water molecules. Subsequently, the FLG and the powder are heated for 7.5 hours at 360°C and 310°C, respectively. A heating rate of 10 °C/min is used during the warming and cooling of the two zones. The powder is cooled first to avoid FeCl$_3$ condensation on the substrate.

Figure 2.4: A scheme of a furnace for the two-zone method of FeCl$_3$ intercalation into FLG. A glass tube is placed inside the furnace so that the FeCl$_3$ powder has slightly higher temperature than the substrate with FLG. The tube is connected to a diffusion pump.

2.2 Contrast determination of the number of layers of FLG

The optical contrast between FLG flakes and the Si/SiO$_2$ substrate is an efficient and well-established method to identify the number of graphene layers [82, 83]. The visibility of FLG is an interference effect because the FLG flake, SiO$_2$ and Si form a Fabry-Perot cavity. Therefore contrast can be maximized by using the appropriate thickness of the SiO$_2$ layer and the light wavelength. The best contrast of 6% for MLG is achieved on a 285 nm thick SiO$_2$ using green light (550 nm). The contrast of FLG increases proportional to the number of layers $N_L$ for not too thick flakes ($N_L \lesssim 10$) [83].

Our experiments are based on FLG deposited on both Si/SiO$_2$ and 100 μm thick glass substrates. The thickness of FLG on Si/SiO$_2$ was determined following the technique described above. Contrary to FLG on Si/SiO$_2$, the contrast of FLGs deposited on glass varies only slightly with the wavelength of light. Therefore the thickness of FLG on glass was determined by analyzing the intensity of the FLG optical micrographs taken with white light (see Figure 2.5a). Figure 2.5b shows the optical contrast $C$
of FLG on glass, where $C = (I_f - I_s)/I_s$ 100% is the relative shift of the intensity of the flake ($I_f$) with respect to the intensity of the substrate ($I_s$). It is apparent that step-like changes are visible with increasing optical contrast. As we will show below, Raman spectroscopy demonstrates that each step corresponds to an increase of the number of layers by 1. This method is accurate for flakes thinner than 5L. For 5L and thicker flakes the contrast measurements have to be complemented by an independent method. Therefore we use Raman spectroscopy. The next section describes the basic principles of this method of sample characterisation.

![Figure 2.5: a. Optical microphotograph of several FLG flakes on a glass substrate. One can see a clear difference in the visual contrast. b. Optical contrast $C$ of an ensemble of FLG flakes on glass. A step-like character of contrast is apparent for $C < 20\%$. Each step is attributed to an increasing number of layers.](image)

### 2.3 Raman spectroscopy

Raman scattering is the inelastic scattering of light by a medium, when spectral lines not present in the incident light are generated in the spectrum of scattered light. The diagram in Fig. 2.6a illustrates the simplest first order non-resonant Raman scattering process. An incoming photon with frequency $\omega_0$ excites an electron to a virtual state creating an electron-hole pair. The electron is then scattered inelastically by emitting a phonon with frequency $\omega_{ph}$ (Stokes scattering). Then the electron-hole pair recombines emitting a photon with the frequency $\omega_1 = \omega_0 - \omega_{ph}$ (red shift). The photon frequency shifts to the blue part of spectrum if the excited electron absorbs a phonon instead of emitting it (anti-Stokes scattering). The Stokes and anti-Stokes spectra often have a symmetric set of frequencies above and below the incident photon frequency. If
one (or both) of the virtual excited states is replaced by a real state (states) then
the process is single-resonant, SR (double-resonant, DR), as in Fig. 2.6b (Fig. 2.6c
correspondingly). The processes shown in the Fig. 2.6 involve only one scattering
event for the excited electron and thus are called first order scattering. High-order
processes are also possible, including scattering of electron by two phonons or elastic
scattering mediated by defects combined with the phonon scattering.

Raman frequency shifts are equal to phonon energies therefore they tell us about
the structure of scattering material. The equipment employed for Raman spectroscopy
is relatively cheap and easy to operate which makes this technique a very useful one for
chemical and structural analysis. Practically one works with the Stokes spectrum as
its lines are much more intensive. Raman shifts are usually expressed via wavelengths
of excitation and scattered light as $\Delta\omega (cm^{-1}) = \left(\frac{1}{\lambda_0(nm)} - \frac{1}{\lambda(nm)}\right) \cdot 10^7$.

2.3.1 Raman spectroscopy of graphene

Raman spectroscopy for graphene has been developed in details and summarised in
reviews [84,85]. The peculiar gapless electron dispersion relation of the $\pi$ electrons in
graphene and FLG makes Raman scattering in these materials to be always resonant.
Thank to this feature it is possible to probe electronic properties of graphene as well
as vibrations.

In order to understand the structure of mono- and FLG Raman spectra let us
consider the phonon dispersion relation of monolayer graphene (Fig. 2.7) [86]. It
has 6 phonon bands: three acoustic branches (transverse (TA), longitudinal (LA) and
flexural (FA) phonons) and three optical branches (transverse (TO), longitudinal (LO)
and flexural (FO)). Flexural vibrations are alternatively called out-of-plane phonons,
whereas transverse and longitudinal vibrations are in-plane. TO and LO phonons in the zone center (Γ point), LO phonons in the vicinity of Γ point and TO phonons in the vicinity of K point are of particular interest because these phonons are Raman active. It is worth noticing that due to the Kohn anomaly [86] TO phonons near K point are softened and highly dispersive. As we will see below this causes dependence of the shift of certain Raman bands on the energy of the excitation light.

When considering the phonon dispersion relations for FLGs and graphite one notices their similarities to the dispersion of monolayer graphene. This is caused by the strong intralayer force constants relative to interlayer force constant [30]. The main difference is the splitting of phonon bands which, for example for TO, is approximately 6 cm$^{-1}$ for graphite [30] and 1.5 cm$^{-1}$ for bilayer graphene [87]. These shifts do not significantly affect our Raman analysis. This problem is beyond the aim of this thesis and therefore we will assume the phonon dispersion of FLG to be the same as for monolayer graphene.

Now let us proceed to the Raman spectra of MLG, where the most important features are the G-band at 1585 cm$^{-1}$ and 2D-band at 2700 cm$^{-1}$ (See Fig. 2.8a, where the spectra are taken at the laser excitation wavelength 532 nm (2.33 eV)). The latter one is sometimes referred to as G’-band [85]. G and 2D bands are always present in the graphene Raman spectrum. In addition to those one can observe a
disorder-induced D-band at 1350 cm\(^{-1}\) in a disordered sample or at the edge of a normal sample, as well as D' and 2D' peaks at 1620 cm\(^{-1}\) and 3250 cm\(^{-1}\).

Figure 2.8: a) The Raman spectra of MLG, BLG, TLG, 10-L graphene and graphite. The plots are shifted vertically for clarity. One can see the increase of the intensity of the G-peak with increase of thickness and trace the evolution of the shape of the 2D-band. b) 2D-band of BLG fitted with four single-peaks. c) 2D-band of TLG fitted with six single-peaks.

The diagrams for the corresponding spectral processes are shown in Fig. 2.9 [85]. The G-band is due to the first-order SR process which is associated with the double-degenerate TO and LO phonon exactly at the Γ point. The D band is due to the second-order DR process involving one electron inter-valley scattering by a defect and then scattering back by TO phonon near the K point. Similarly, the D' band is due to the second-order DR process involving one electron elastic intra-valley scattering by a defect or an impurity and then inelastic scattering back by LO phonon near the Γ point. D and D' processes require a defect for their activation and are not present in the spectra of clean and ordered samples. 2D and 2D' bands are also due to second-order double-resonant processes similar to D and D' processes. The difference is involvement of two phonons instead of a combination of a phonon and an impurity scattering. Therefore the Raman shifts of 2D and 2D' bands are approximately twice of the corresponding shifts of the D and D' bands.

There are three remarkable properties of the 2D band of monolayer graphene. First,
it has a single-peak symmetric shape as one would expect from the diagram in Fig. 2.9. Second, its Raman shift linearly depends on the energy of the excitation light. The explanation of this phenomenon is the following. When the excitation energy $E_{ex}$ is increased, the resonance $k$ vector for the electron moves away from the K point. The corresponding $q$ vector of the phonon increases as well, as can be seen from Fig. 2.9. Thus by changing $E_{ex}$ we can observe the phonon energy $\hbar \omega(q)$ along the phonon dispersion relation. Thanks to the Kohn anomaly [86] the TO phonon has an enhanced dispersion near the K point (See Fig. 2.7) and this effect is easy to observe. The third peculiarity of the 2D peak of MLG is its increased height compared to the height of the G band. One of the explanations for this fact is the possibility of a triple-resonance (TR) process shown in Fig. 2.9 in parallel with the DR process [85]. The former process is possible because the conduction and valence bands of MLG are almost perfect mirror reflections of each other.

Let us now consider the Raman spectrum of BLG (Fig. 2.8a). Like the MLG spectrum it has G and 2D bands at the shifts about 1585 cm$^{-1}$ and 2700 cm$^{-1}$. The 2D-band acquires a multi-peak structure which can be fitted with four peaks (Fig. 2.8b). The explanation for such structure lies in the electronic dispersion relation of BLG (Fig. 2.10), in which conduction and valence bands are split in two each. Therefore there are four possible electron-hole excitations, each having two alternatives for
Following intervalley transitions via scattering with a TO phonon near the $K$ point. According to the DFT calculations [84] light couples more strongly to the electron transitions between the same subbands, leaving only 4 processes shown in Fig. 2.10. These processes have slightly different phonon wavevectors $q$ and thus due to the sharp TO phonon dispersion relation near $K$ point, slightly different Raman shifts.

One can conduct similar analysis for TLG for which the Raman spectrum also has the 2D-band at 2700 cm$^{-1}$. The result of the analysis gives 15 possible transitions, although many of them have close Raman shifts [88]. In practice one fits trilayer 2D-band with a minimum of six peaks, as shown in Fig.2.8c. The G-band of TLG has the same single-peak structure as that of MLG or BLG but with an increased peak height.

The 2D-band evolves with the increasing number of layers until it becomes indistinguishable from the 2D band of graphite at approximately $N_L=10$ layers (Fig. 2.8a) [89]. The G-band also progressively changes increasing its intensity $I_G$, although $I_G$ saturates to the value corresponding to bulk graphite after $N_L>10$.

### 2.3.2 Determination of the number of layers of FLG using Raman spectroscopy

All the Raman spectra presented in this thesis are collected in ambient air and at room temperature with a Renishaw spectrometer. An excitation laser with a wavelength of
532 nm, focused to a spot size of 1.5 µm diameter and a ×100 or ×50 objective lens are used. To avoid sample damage or laser induced heating, the incident power is kept at 5 mW.

Following [90] we explore the well-known property of FLGs to increase the intensity of the G-band with the number of layers \( N_L \). The method we refer to was applied to FLG on Si/SiO\(_2\) substrates and utilises a Si peak at the Raman shift \( \sim 519 \text{ cm}^{-1} \) as a reference peak. In order to use this method for FLG on glass we placed the glass substrate on top of a SiO\(_2\)/Si substrates with the FLGs facing the surface of the SiO\(_2\) (see Figure 2.11a). Figure 2.11b shows \( I_G/I_Si \) for FLG with different \( N_L \) determined from the optical contrast. As expected, \( I_G/I_Si \) values break into groups and increase monotonically with increasing \( N_L \).

![Figure 2.11](image_url)

Figure 2.11: a) A schematic view of a glass substrate on top of a Si/SiO\(_2\) substrate. The face of the glass substrate which has the FLG flakes is down. b) G-peaks of FLGs of different thicknesses (determined from optical contrast). The spectra are shifted horizontally for clarity. Each double line corresponds to two samples. It is apparent that the method is not quite reliable for FLG thicker than 5-layer.

Each Raman spectrum has a background coming, for example, from the substrate or surface contamination. This background varies from sample to sample, irregularly depends on the wavenumber and introduces a significant error to our results. Therefore before the interpretation of the Raman spectra we always subtract the background separately for each peak. Also, the G peak intensity may vary slightly from sample to sample because of uncontrolled variation in the beam focusing, SiO\(_2\) thickness or some other factors which may not to be known to the author. This is why the G-band intensities are normalised to the Si-peak to exclude this error. This method allows one to distinguish between FLGs 5 to 7 layers thick (depending on whether FLG is deposited on top of glass or Si/SiO\(_2\) substrate respectively).

In order to confirm the number of layers we also examine the evolution of the shape
of the 2D-band as well. We find it intricate and not reliable to fit the 2D-bands with a number of single peaks for the FLG thicker than trilayer. Instead we compare the shapes of the 2D-bands of a statistical ensemble of samples without specifying the details of their structure. For doing that we suggest the following procedure (See the example in Fig. 2.12):

1. The background in the vicinity of the 2D-band is subtracted for each spectrum (Fig. 2.12b).

2. The maximal intensity of each 2D-band is normalised to 1 (Fig. 2.12c). Here we do not use the ratios $I_{2D}/I_S$ because the height of the 2D band is known to depend on the individual sample characteristics such as doping [90].

3. After the step 2 all the spectra are equally high but still have slight difference in the Raman shift in the vicinity of 2700 cm$^{-1}$. Therefore for each spectrum we define two wavenumbers where the normalised intensity is equal to 0.5 and set one of these wavenumbers (say, the higher one) to be zero (Fig. 2.12d). This procedure is one of the possible ways to move all the spectra to a common origin.

![Figure 2.12: a) 2D-bands of the Raman spectra of a number of FLG flakes. b) The same spectra after the background is removed. c) All the peaks are normalised to the height equal 1. d) The grouping of the spectra according to the thickness of the flakes becomes apparent after the right half-maxima of all the bands are shifted to the same origin.](image-url)
At the end we can see that all the spectra break into several groups. The number of layers in Fig. 2.12 is assigned from the optical contrast measurements.

2.4 Electrical characterisation and current annealing

Within this work we perform electrical characterisation of supported FeCl$_3$-FLG in the low-bias regime at the range of temperatures between 0.245 K and 300 K. The measurements are done in 4-probe configuration and constant current regime (See Fig. 2.13 for the measurement circuit) with the typical ballast resistance of $R_B=1$ MΩ. Typically the resistance of our samples is of order of $\sim 1$ kΩ for pristine FLG and $\sim 10$Ω for intercalated FLG. Therefore the sample resistance does not affect the current value $I = V_{osc}/R_B$. The longitudinal $V_{xx}$ and transverse $V_{xy}$ voltages are measured with a lock-in amplifier. The excitation a.c. current $I$ is varied to ensure that the energy range where electrical transport takes place is smaller than the energy range associated with the temperature of the electrons: $eV_{xx} < k_BT$. This prevents heating of the electrons and the occurrence of nonequilibrium effects.

![Figure 2.13: Experimental setup for the low-bias measurements.](image)

In order to perform SdHO analysis the measured resistance $R_{xx} = V_{xx}/I$ is transformed to the resistivity $\rho_{xx}$ and then to the conductivity $\sigma_{xx}$ via inverting the resistivity matrix: $\sigma_{xx} = \rho_{xx}/(\rho_{xx}^2 + r\rho_{xy}^2)$.

Measurements of the $R(V_G)$ characteristics of suspended FLG samples are performed in the low-bias regime at a temperature of 4.2 K. The measurements are done in 2-probe configuration and constant current regime with the typical ballast resistance of 10 MΩ. Typically the resistance of the suspended samples is less than 10 kΩ. Gate
voltage is used to control the carrier concentration via electrostatic doping \( n = CV_G \). For supported graphene on a \( d_0=300\text{nm} \) thick layer of SiO\(_2\) the coefficient \( C \) is equal \( C_0 = 7.2\times10^{10} \text{cm}^{-2}\text{V}^{-1} \) [3]. In case of suspended graphene it is equal \( C = C_0 \frac{d_0}{d_0+(\varepsilon-1)d_{\text{gap}}} \) with \( d_{\text{gap}} \) being the gap between graphene membrane and SiO\(_2\) and \( \varepsilon \) being the dielectric permittivity of SiO\(_2\). Here the plain capacitor model is valid as long as the geometry of the system does not depend on the applied gate voltage. This model is valid in our experiments with suspended samples because we use low \( V_G \sim 10\text{V} \) which is not high enough to stretch FLG membrane significantly [18].

At \( V_G=0 \) the carrier concentration of clean graphene is zero. A real sample always has a certain amount of contamination causing finite chemical doping. Therefore the neutrality gate voltage \( V_{NP} \) is different from zero. Practically one defines \( V_{NP} \) as the voltage at which \( R(V_G) \) has its maximum (see Fig. 1.5). Taking into account the chemical doping the carrier concentration is equal \( n = c(V_{NP} - V_G) \).

The measurement set-up for pulsed annealing of suspended FLG differs from the set-up described above (See Fig. 2.14a). In particular, instead of a ballast resistor we use an RC-filter with each resistance equal \( R = 10\text{k}\Omega \) and each capacitance equal \( C = 10\mu\text{F} \). By means of the filter we avoid current spikes which can damage graphene flakes when we apply voltage steps from the source. After the settling time of order of \( \tau = RC = 0.1\text{s} \) the filter acts as a ballast resistor with \( R_B=30\text{k}\Omega \) (see current step-response curve in Fig. 2.14b). Typically the resistance of our samples at high bias is of order of 1 k\( \Omega \). This affects the current value and, hence, we measure both voltage across sample and current to be able to extract the sample resistance.

![Figure 2.14: a) Experimental setup for the current annealing experiments for suspended graphene. b) Current step-response of the RC-filter used in the experiments.](image-url)
Chapter 3

Structure study of FeCl$_3$-intercalated graphene

3.1 Introduction

In this chapter we provide the detailed study of the structure of FeCl$_3$-FLG. We base our analysis on the Raman spectroscopy and electrical transport measurements in high magnetic field. We show that FeCl$_3$ molecules intercalate few-layer graphene, penetrating between graphene planes and decouple electrically the hole gases present in each layer. We provide a comprehensive methodology which enables us to define the intercalation staging and make conclusions on the uniformity of the resulting compound. The choice of the Raman and electrical transport measurements for structural analysis is caused by the small thickness of FeCl$_3$-FLG and substrate effects. These make it difficult to apply direct structural determination techniques (for example X-ray diffraction) to our samples.

3.2 Raman study

FeCl$_3$-intercalation changes the Raman spectrum of few-layer graphene in two distinctive ways: symmetrisation of the 2D-band and shift of G-band accompanied with its splitting. It should be noticed that we could not detect any D-peak after the intercalation. Therefore we conclude that the graphene hexagonal structure was not damaged. Thus we can focus on the intercalation staging of the resulting material.

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Figure 3.1: The G and 2D Raman bands of pristine FLG (a) and of FeCl₃-FLG (b) with different thicknesses ranging from 2L to 5L. One can notice the conversion of asymmetric 2D-band into symmetric one under intercalation. The Raman shift of G to G1 and G2 stem for a graphene sheet with one or two adjacent FeCl₃ layers as shown by the schematic crystal structure in Fig. 3.2a,b.

Fig. 3.1a shows the 2D-band of pristine bilayer and thicker graphene. The band has an asymmetric shape which results from its multi-peak structure. In contrast, the 2D-band of a monolayer graphene has the single-peak structure, as discussed in the Chapter 2 (Fig.2.8). After processing of 3-, 4- and 5layers in the furnace we observe degeneration of the 2D-band into a single peak (Fig. 3.1b). This indicates that individual graphene planes become decoupled from each other and therefore they act as independent monolayers in the Raman scattering process. Fig. 3.1b also demonstrates that the G-band shifts and splits supporting formation of several independent monolayers.

The most detailed information which can be obtained from the Raman spectra is the intercalation stage. It is defined by the shape of the G-band. For all four- and five-layer intercalated graphene samples we observe duplet component of the G-band with maxima at \(\sim 1613 \text{ cm}^{-1}\) (\(G_1\) peak) and \(\sim 1625 \text{ cm}^{-1}\) (\(G_2\) peak). The \(G_1\) peak corresponds to a graphene sheet with only one adjacent intercalant layer [30] as shown in Fig. 3.2a. The \(G_2\) peak represents higher doping level and characterises a graphene sheet sandwiched between two FeCl₃ layers [30] (See Fig. 3.2b). The upshift in frequency of the \(G_1\) and \(G_2\) peaks relative to \(G_0\) peak of pristine FLG is due to the difference in the force constants arising from the different environment of the carbon
atoms. The simultaneous presence of $G_1$ and $G_2$ peaks suggests the structure shown in the Fig. 3.2c. This structure has been reported previously in \cite{53} and corresponds to intercalation stage I of bulk graphite. The $G_1$ peak is always present in the spectra, and we attribute this to the acetone washing which removes the top layer of FeCl$_3$. This causes the top graphene plane to have only one adjacent layer of FeCl$_3$ \cite{30}. The washing can also cause removal of the bottom layer of FeCl$_3$ between the flake and the substrate \cite{55} as well as partial deintercalation of internal layers of FeCl$_3$.

Figure 3.2: a) A graphene plane with only one adjacent intercalant layer is responsible for the $G_1$ peak in the Raman spectrum of FeCl$_3$-FLG. b) A graphene plane with intercalant layers present at each side has higher doping level and is responsible for the $G_2$ peak. c,d) Structures of FeCl$_3$-4L and FeCl$_3$-3L corresponding to simultaneous presence of $G_1$ and $G_2$ peaks and absence of $G_0$ peak, as in the spectra in the Fig. 3.1b. e) Minimal graphite intercalation compound - the structure of FeCl$_3$-2L corresponding to the $G_0$ peak only present in the Raman spectrum.

Double-peaks were reported previously for higher than intercalation stage II of graphite \cite{30}. In those cases G-peaks had positions below 1585 cm$^{-1}$ ($G_0$) and below 1608 cm$^{-1}$ ($G_1$) with no peaks close to the position of $G_2$. In contrast, for our samples $G_2$ is the principal peak while $G_0$ is often not present or small (see the analysis below). Therefore the double-peak structure of the G-band itself is not a proof of the intercalation stage II and the frequency of every peak should be carefully taken into account.
Chapter 3: Structure study of FeCl$_3$-intercalated graphene

Figure 3.3: Raman spectra of non-uniformly intercalated 3L (a), 4L (b) and 5L (c) graphene samples. In each case the spectrum is taken at several points. The data indicate that many FeCl$_3$-FlG samples have a partially de-intercalated top layer of FeCl$_3$ as it is shown in Fig. 3.4.

Several of our four- and five-layer samples exhibit a triplet G-band with a small additional maximum below 1590 cm$^{-1}$ (G$_0$ peak). This Raman shift corresponds to pristine graphene [30,54] (which implies at least one free graphene plane in the structure). Samples having the G$_0$ peak can be divided into two groups. In the first group the height of this peak is dependent on the position of the laser spot on the flake (See Fig. 3.3b,c). In this case we attribute the G$_0$ peak to occasional discontinuity of the top layer of FeCl$_3$ between two outermost planes of graphene. In other words, this indicates the presence of patches on the flake surface with the top plane of graphene free of FeCl$_3$ as shown in Fig. 3.4. Another group of samples with the triplet G-band exhibits the uniform intensity of G$_0$ peak (Fig. 3.5). This implies that there is at least one graphene plane completely free of FeCl$_3$. In this case the exact structure is clarified by means of magnetoresistance study as will be shown below.

Figure 3.4: The structure of FeCl$_3$-FlG with partially de-intercalated top layer of FeCl$_3$.

Now let us consider FeCl$_3$ trilayer graphene. Certain trilayer samples exhibit G$_1$ and G$_2$ peaks of approximately equal height with no G$_0$ peak and little spatial variation of the spectrum (Fig. 3.1b). This suggests the structure shown in Fig. 3.2d [53]. At the same time intercalation of most of trilayer flakes was not uniform (Fig. 3.3a)
Figure 3.5: Raman spectrum of a chosen FeCl$_3$-5L with G$_0$ peak. Spectra taken in 10 different locations coincide pointing to a uniform structure different from the one shown in Fig. 3.2c.

with dominant G$_1$ peak in the Raman spectrum and occasional G$_0$ and G$_2$ peaks. This spectrum takes place if at least one of intercalant layers is discontinuous. This discontinuity together with the absence of adsorbed layer of FeCl$_3$ is possibly due to the washing of samples in acetone during the fabrication or to an incomplete intercalation process. Authors of [55] faced similar problems.

The results of intercalation vary depending on the shape of the flake, quality of FeCl$_3$ powder used and alterations of the fabrication process. As in the example in the Fig.3.3 above the Raman spectrum of many flakes depends on the laser spot position. The spectra in the Fig. 3.3 are scaled so that for a given flake the height of the most pronounced peak is the same for all positions. It should be noticed that for the four- and five-layer devices we can see a trend in the spectra as in the Fig. 3.3b,c. Thus we consider the non-homogeneity as a deviation from the trend shown in Fig. 3.1. For most of the trilayers there are no obvious trends.

Although a number of FeCl$_3$-bilayer graphene flakes exhibit Raman spectra corresponding to the stage II intercalation (See Fig. 3.1e for the spectrum and Fig. 3.2d for the structure), for most of intercalated bilayer graphene samples we observe no symmetrisation of 2D peak together with the small shift of G peak within limits of frequency of G$_0$ peak. Therefore doping without structural changes takes place in these samples.
Chapter 3: Structure study of FeCl$_3$-intercalated graphene

3.3 Shubnikov-de Haas oscillations

3.3.1 Determining the carrier concentration from the frequency of the oscillations

Raman spectroscopy alone can accurately define the structure of FeCl$_3$-FLG only for bilayer graphene. In order to characterise thicker FeCl$_3$-FLG, we study its transport properties. We pattern Cr/Au contacts in the Hall bar configuration using electron-beam lithography (See Fig. 3.6). We use transparent glass substrates for a significant part of our devices and hence we do not have an opportunity to change carrier concentration by means of electrostatic gate. However we have produced several test devices on the traditional Si/SiO$_2$ substrates to ensure that the substrates have no significant effect on the transport properties. For the samples on Si/SiO$_2$ substrates we found the gate-induced variation of the resistance to be negligible. This is because the charge modulation accessible with SiO$_2$ gate dielectric is limited to $\sim 10^{13}$ cm$^{-2}$ which is small compared to the doping level of these FeCl$_3$ intercalates FLGs ($\sim 10^{14}$ cm$^{-2}$).

![Figure 3.6: False color optical microscope image of an intercalated Hall bar device.](image)

In order to estimate the carrier concentration induced by FeCl$_3$ intercalant we measured the Hall resistance across our samples in weak magnetic field ($B < 2$ T) at 4.2 K (Fig. 3.7). The linear dependence of $R_{xy}(B)$ with positive slope identifies the charge carriers as holes and the Hall carrier density $n_H = B/(eR_{xy})$ ranging between $3 \cdot 10^{14}$ cm$^{-2}$ and $8.9 \cdot 10^{14}$ cm$^{-2}$ for the 3- to 5-layer samples. The measured Hall carrier concentration is close to the charge transfer of $5.6 \cdot 10^{14}$ cm$^{-2}$ per graphene plane of
intercalated graphite. One can see a significantly higher slope of $R_{xy}$ for the representative bilayer sample in Fig 3.7. The slope corresponds to the Hall carrier concentration equal to $2 \cdot 10^{12}$ cm$^{-2}$, two orders of magnitude smaller compared to the level of doping obtained for thicker graphene. The Hall measurements confirm the conclusion based on the Raman data that processed bilayer graphene is doped, which means that no intercalant molecules are present between graphene planes.

![Diagram](image)

Figure 3.7: Hall resistance of FeCl$_3$-FLG as a function of magnetic field. The inset shows the data for the bilayer sample on a smaller B scale. Panels b) and c) show the carrier density and mobility for FeCl$_3$-FLG as a function of the number of graphene layers.

### 3.3.2 Determining the cyclotron mass from the temperature decay of the oscillations

As it was shown in the Section 1.3.2 (See Eq.1.38), the Hall carrier concentration $n_H = (\Sigma n_i \mu_i)^2/\Sigma n_i \mu_i^2$ differs from the total carrier concentration $n_{tot} = \Sigma n_i$ (with $n_i$ and $\mu_i$ the carrier density and mobility of each separate hole gas). The first one is smaller and gives an estimate of the order of magnitude of the latter one. A more detailed insight to the total carrier concentration and the number of hole gases is achieved by the analysis of the Shubnikov-de Haas (SdHO) oscillations of longitudinal magnetoconductance $G_{xx}$ in a perpendicular magnetic field. We show the representative data for an intercalated 5L sample at several temperatures in Fig. 3.8a. In order to perform
the analysis we consider the conductance as a function of inverse magnetic field (See the inset in Fig. 3.8b).

Figure 3.8: a) Longitudinal conductance \( G_{xx} \) as a function of magnetic field at different temperatures (curves shifted for clarity). b) Fourier transform of \( G_{xx}(1/B) \) with peaks at frequencies \( f_1 = 1100T \) and \( f_2 = 55T \). The inset shows \( G_{xx} \) as a function of inverse magnetic field at different temperatures (curves shifted for clarity).

It is apparent that for \( T < 10 \) K \( G_{xx} \) oscillates with two distinct frequencies. For \( T > 10 \) K only the lower frequency oscillations are visible. This means that electrical conduction takes place via several parallel hole gases with different densities and cyclotron masses. Fourier transformation of these oscillations yields peaks at high frequency \( f_1 = 1100T \) and low frequency \( f_2 = 55T \) (Fig. 3.8b). The corresponding carrier concentration \( n_1 = \frac{4e}{h}f_1 \) (See Eq.(1.31) in the Section 1.3.1) is equal \( 1.1\cdot10^{14} \) cm\(^{-2}\) for the high frequency and represents concentration of hole gases of graphene planes sandwiched by FeCl\(_3\) layers (Raman shift of 1625 cm\(^{-1}\)). Carrier concentration calculated for the low-frequency oscillations is \( 5.5\cdot10^{12} \) cm\(^{-2}\) and represents doped layers with one or no adjacent intercalant layers.
Figure 3.9: The low- (a) and high- (b,c) frequency magneto-conductivity oscillations vs $1/B$ extracted from the measurements in Fig. 3.8a.

The analysis of the temperature decay of SdHO is a tool to find the cyclotron mass of the charge carriers [81, 91]. We separate oscillations at two different frequencies to be able to perform this analysis accurately. Since conductances of parallel resistors are additive, firstly we convert the measured resistivities to longitudinal conductivity $\sigma_{xx} = \rho_{xx}/(\rho_{xx}^2 + \rho_{xy}^2)$ (with $\rho_{xx}$ and $\rho_{xy}$ the longitudinal and transversal resistivity, respectively). At the second step we average out the high frequency oscillations. The result has only the low frequency oscillations (Fig. 3.9a). At the third step we subtract
these oscillations from the total resistance and obtain the high frequency oscillations (Fig. 3.9c). The beating visible in Figure Fig. 3.9c is the signature of several oscillations at close frequencies. Therefore there is more than one hole gas of high density. We separate the high and low frequency oscillations for a variety of temperatures to get the temperature-dependence of the SdHO. Then, at the final step we plot the temperature dependence of the oscillation amplitude at an arbitrary magnetic field (Fig. 3.10a). At the end the amplitude decay is fitted with the formula $A(T) \propto \frac{T}{\sinh(2\pi^2 m_c k_B T / e h B)}$ [80] where the cyclotron mass is the only fitting parameter. The resulting masses are $0.08 m_e$ for the low-frequency oscillations and $0.27 m_e$ for the high-frequency oscillations.

![Figure 3.10](image)

Figure 3.10: a) Temperature decay of the amplitude ($A$) of $\Delta \sigma_{xx}$ oscillations at $B = 6.2T$. The amplitudes are normalized to their values at $T = 0.25K$. The continuous lines are fits to $A(T)/A(0.25)$ with the cyclotron mass $m_c$ as the only fitting parameter. b) Schematic crystal structure of a 5L FeCl$_3$-FLG in which electrical transport takes place through four parallel conductive planes, one with bilayer character and three with monolayer character.

### 3.3.3 Character of graphene planes coupling from comparison of mass and carrier concentration

Now we can correlate the cyclotron masses of the charge carriers with the densities of the gases they form. We find that the cyclotron mass of holes equal $(0.25 \pm 0.05)m_e$
which is consistent with the high carrier concentration if we assume the holes to be massless Dirac fermions like in pristine monolayer graphene. In this case at the carrier concentration of $n_1$ the cyclotron mass is $m_c = \sqrt{\hbar^2 n_1/4\pi v_F^2} = 0.21 m_e$ in agreement with our experiments. The use of the same equation for the low carrier concentration of $n_2$ yields the cyclotron mass of $0.045 \cdot m_e$ which is not in agreement with the corresponding experimental value of $(0.08 \pm 0.01) m_e$. However if we assume the holes to be massive particles like in pristine bilayer graphene, where $m_c = \sqrt{\hbar^2 v_F^2 \pi n_2 + (\gamma/2)^2 / v_F^2} = 0.084 m_e$, the observed cyclotron mass of holes of $0.08 \cdot m_e$ does agree with the low carrier concentration $n_2$.

The number of parallel gases can be readily identified by correlating SdHO to the Hall resistance measurements. The Hall carrier concentration for this sample is $n_H = 3 \cdot 10^{14}$ cm$^{-2}$. The total carrier concentration $n_{tot} = \Sigma n_i$ should be higher than the Hall carrier concentration $n_H = (\Sigma n_i)^2 / \Sigma n_i \mu_i^2$ [92]. We can see that only a minimum of three parallel gases with $n \sim 1.1 \cdot 10^{14}$ cm$^{-2}$ can explain the value of $n_H$, namely $3 \cdot n_1 + n_2 \geq n_H$. Therefore, the electrical transport characterisation demonstrates the presence of four parallel hole gases, of which one gas is due to two coupled graphene planes and three gases correspond to a monolayer sheet each. This conclusion is in agreement with the Raman spectrum of this particular device Fig.3.5b showing the presence of G$_0$, G$_1$ and G$_2$ peaks. A schematic of the structure is presented in the Fig. 3.10b. The bilayer gas is most likely to be caused by two top layers of the stacking which have been de-intercalated possibly due to rinsing in acetone during lift-off.

In total we have investigated electrical transport and Raman spectroscopy in eight samples, of which four are 5-layers. In all cases we confirmed the structure similar to the one in Fig. 3.10b. In the next chapter we show how this structure defines optical transparency and electrical conductivity of FeCl$_3$-FLG.
Chapter 4

Intercalated graphene as a transparent conductor

4.1 Introduction

In this chapter we present the data on the electrical resistivity of FeCl$_3$-FLG. The dependence of the resistivity on temperature and number of layers, as well as the effect of the non-uniform top layer of intercalant on the electrical transport is discussed. We also show that FeCl$_3$-FLG is almost as transparent as pristine graphene. This, in combination with superior electrical properties and stability of the material in air, makes it promising for optoelectronic applications as a replacement for commonly used indium-tin oxide (ITO).

4.2 Sheet resistance of the FeCl$_3$-FLG

In order to compare FeCl$_3$-FLG to other transparent conductors we will need to use the concept of square resistance (or, according to some authors, sheet resistance) [37]. Sheet resistance of a sample is the resistance of the sample $R$ divided by the ratio of its length $L$ to width $W$: $R_s = \frac{R}{L/W}$. If a sample would have the square shape its resistance would be equal to the square resistance and would not depend on the size of the square. Thus $R_s$ is a convenient characteristics to compare different thin films and planar structures as conductors. In case of a 2D electron or hole gas the sheet resistance coincides with the resistivity: $R_s = \rho_{2D}$. If a material contains several 2D gases the
sheet resistance is found from the condition of parallel conduction: \(1/R_s = \Sigma 1/\rho_{2D_i}\), or, in case of \(N\) identical gases \(R_s = \rho_{2D}/N\). For a bulk 3D conductor \(R_s\) depends on the sample thickness and resistivity \(\rho_{3D}\): \(R_s = \rho_{3D}L/(hW) = \rho_{3D}/h\). Summary of these three cases is given in Tab. 4.1

<table>
<thead>
<tr>
<th>Relation between (R_s) and (\rho)</th>
<th>2D gas</th>
<th>(N) identical 2D gases</th>
<th>3D bulk material</th>
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<tbody>
<tr>
<td>Dimension of resistivity</td>
<td>(\Omega)</td>
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<td>(\Omega m)</td>
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Table 4.1: Relation between the square resistance \(R_s\) and the resistivity \(\rho\)

A remarkable property of FeCl\(_3\)-FLGs shown by the electrical transport characterization is that intercalated materials thicker than 3L exhibit a very low sheet resistance. We find a room temperature value of \(R_s = 8.8\Omega\) in our best 5L intercalated FLG. The 4L intercalated FLGs typically exhibit higher sheet resistance values of approximately \(R_s = 20\Omega\) which is, however, an extremely low value. Figure 4.1a shows a comparison between the electrical properties of several 4L and 5L intercalated FLGs devices.

![Graph showing comparison between electrical properties of 4L and 5L FeCl\(_3\)-FLG](image)

Figure 4.1: a) Room temperature square resistance for 4L and 5L FeCl\(_3\)-FLG. b) Temperature dependence of the square resistance for 4L and 5L FeCl\(_3\)-FLG. c) Raman spectra of 4L and 5L FeCl\(_3\)-FLG devices.

Furthermore, we have measured the temperature dependence for 3 intercalated 5L samples and they all show lower sheet resistance than the 4L samples over all the investigated temperature range (See Fig. 4.1b). Figure 4.1c shows that typical Raman spectra of 4L intercalated FLGs devices is similar to the one of 5L intercalated devices, i.e. they both show the presence of pristine \(G_0\), \(G_1\) and \(G_2\) peaks. This suggests that 4L and 5L intercalated devices have similar crystal structures. The sheet resistance of FeCl\(_3\)-FLGs thicker than 2L decreases when lowering the temperature as expected for metallic conduction (Figure 4.1a). Contrary to intercalated samples, pristine FLGs
always have two orders of magnitude higher $R_s$. Their resistance exhibits non-metallic behaviour as a function of temperature \cite{77, 93, 94} (Figure 4.1b).

![Graph showing temperature dependence of square resistance for FLG intercalated with FeCl$_3$ and pristine FLG](image)

Figure 4.2: a) Temperature dependence of the square resistance for FeCl$_3$-FLG of different thicknesses. b) Square resistance for pristine FLG of different thicknesses as function of temperature. These devices are fabricated on SiO$_2$/Si substrates and the highly-doped Si substrate is used as a gate to adjust the Fermi level to the charge neutrality of the system.

This suggests that the origin of the low values of $R_s$ and the metallic nature of the conduction are consequences of intercalation with FeCl$_3$. As we have seen in the previous chapter, the Hall coefficient measurements reveal that $n_H$ of FeCl$_3$-FLGs has values as high as 8.9*10$^{14}$ cm$^{-2}$. These charge densities exceed even the highest values demonstrated so far by liquid electrolyte \cite{95} or ionic \cite{96} gating. At such high doping the Fermi level of monolayer graphene shifts up to 1 eV \cite{53–55}. This value is much higher than the thermal excitation energy at the room temperature (26 meV). Thus intercalated graphene behaves as a metal.

![Diagram showing Hall mobilities](image)

The Hall mobilities (Fig. 3.7c) for the 4L and 5L samples typically range from $\mu_H = 1540$ cm$^2$/V.s to $\mu_H = 3650$ cm$^2$/V.s ($\mu_H = 1/(n_HeR_s)$ with $e$ - the electron charge). Consequently, the charge carriers in thick FeCl$_3$-FLG have a mean free path as high as 0.26 $\mu$m in 5L at room temperature. The outstanding electrical properties, e.g. lower $R_s$ than ITO and macroscopic mean free path, found in FeCl$_3$-FLGs thicker than 3L are of fundamental interest for the development of novel electronic applications based on highly conductive materials.

FeCl$_3$-2L and 3L graphene suffer from partial de-intercalation possibly caused by
the device fabrication procedure, which results in higher $R_s$ values and in a non-metallic behaviour for 2L similar to pristine FLGs (Fig. 4.2a). Although 3L graphene exhibits high average carrier concentration (Fig. 3.7), layers of FeCl$_3$ inside its structure are close to the top and bottom surfaces. Consequently they are discontinuous, as it is revealed by the Raman spectroscopy. Therefore the structure is disordered and electrons in FeCl$_3$-3L experience intensive scattering. As the result the mobility is low ($\sim$74 cm$^2$/Vs), see Fig. 3.7c). FeCl$_3$-2L can have only one internal layer of FeCl$_3$. Therefore it is easier for bilayer graphene to deintercalate almost completely, with low carrier concentration and increased mobility characteristic to pristine bilayer graphene. The common feature of 4L and 5L is the presence of at least one layer of FeCl$_3$ buried inside the structure and protected from deintercalation. This is why in this work we could succeed with making FLG highly conductive by intercalation.

4.3 Optical transmittance spectra of FeCl$_3$-FLG

Whether FeCl$_3$-FLGs can replace ITO in optoelectronic applications strongly depends on their optical properties. Surprisingly, our detailed study of the optical transmission in the visible wavelength range shows that while FeCl$_3$ intercalation affects significantly the electrical properties of graphene, it leaves the optical transparency nearly unchanged.

The transmission of pristine FLG and FeCl$_3$-FLG is characterized by measuring the bright-field transmission spectra. We utilise the system based on an inverted optical microscope (Nikon Eclipse TE2000-U) combined with a spectrometer and charge-coupled device (CCD) camera (Princeton Instruments, SpectraPro 2500i) to acquire data. White light from a tungsten filament lamp is used to illuminate the samples and, after passing through the sample, is collected by a dry Nikon lens (S Plan Fluor ELWD) $\times$40 of numerical aperture 0.60. A slit width of 50 µm is used for the spectrometer, yielding a spectral resolution $<1$ nm for the measurements. In the spectrometer the dispersed light is projected onto the 1024$\times$256 lines of the CCD camera. Data from the camera are extracted to give the transmission spectra of the flake or part of it. Further the data are normalized to the signal obtained through a region of bare substrate. For the visually uniform parts of the flakes, spectra are averaged along several lines of the CCD camera to improve the signal-to-noise ratio.
Figure 4.3 a and b show a comparison between the transmittance spectra of pristine FLG and FeCl$_3$-FLG. The transmittance values of pristine FLG at the wavelength of 550nm are in agreement with the expected values, [49] highlighted in Figure 4.3 a, and with the results reported by other groups [49, 50]. Upon intercalation, the transmittance slightly decreases at low wavelengths however it is still above $T_r = 80\%$. In order to measure an accurate value of transmittance we fit it with a linear dependence on the number of layers for a statistical ensemble of flakes (Figure 4.3 d). This results in similar extinction coefficients per layer for pristine FLG ($\approx 2.4 \pm 0.1\%$) and for FeCl$_3$-FLG ($\approx 2.6 \pm 0.1\%$), see Figure 4.3 c and d. For wavelengths longer than 550nm we observe an increase in the optical transparency of FeCl$_3$-FLGs. This is a significant advantage of our material compared to ITO whose transparency decreases for wavelengths longer than 600nm. [37]. This property provides a potential for the use in applications that require conductive electrodes which are transparent both in visible and near infrared range. For instance, FeCl$_3$-FLG transparent electrodes could be used for solar cells to harvest energy over an extended wavelength range as compared to ITO-based devices, or for electromagnetic shielding in infrared.

### 4.3.1 Stability of the material

Finally, an important characteristic required by a transparent conductor is its stability upon exposure to air. In principle FLGs could be intercalated with a large variety of molecules, similar to the graphite intercalation compounds (GIC) [30]. However, most of the GIC are unstable in air, with donor compounds being easily oxidized and acceptors being easily desorbed. Therefore we studied the stability of FeCl$_3$-FLG in air by performing Raman measurements at different periods of time after fabrication. Fig. 4.4 shows a comparison between Raman spectra collected at different positions on a FeCl$_3$-5L sample, at the day of fabrication (Fig. 4.4a), after keeping the samples for 3 months (Fig. 4.4b) and one year (Fig. 4.4c) in air. It is apparent that the spectra show no appreciable change. This demonstrates the stability in air of FeCl$_3$-FLGs and has important implications for the utilization of these materials as transparent conductors in practical applications such as displays and photovoltaic devices.
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Figure 4.3: Panels a) and b) show the transmittance spectra of pristine FLG and FeCl₃-FLG, respectively. The horizontal lines in b) are the corresponding transmittances at the wavelength of 550nm reported in the literature [49, 50] c) Transmittance at 550nm for pristine FLG as a function of the number of layers. The red line is a linear fit, which gives the extinction coefficient of 2.4 ± 0.1% per layer. d) Transmittance at 550nm for fully intercalated FeCl₃-FLG (FI), partially intercalated FeCl₃-FLG (PI) and doped FeCl₃-FLG (D) as a function of the number of layers. The black line is a linear fit with the extinction coefficient of (2.6 ± 0.1)% per layer.

4.4 FeCl₃-FLG as perspective material for wearable electronics

The high transparency observed in FeCl₃-FLG complemented by their remarkable electrical properties makes these materials valuable candidates for transparent conductors. However, to replace ITO in optoelectronic applications, it is generally agreed that materials must (at least) have the properties of the best commercially available ITO ($R_s=10\ \Omega$ and $Tr=85\%$ [57]). Figure 4.5 compares $R_s$ vs. $Tr$ of FeCl₃-FLG materials with ITO [41] and other promising carbon-based transparent conductors such as carbon-nanotube films [38] and doped graphene materials [50]. It is apparent that $R_s$ of FeCl₃-FLGs is lower than the corresponding value of ITO and of the best values for
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Figure 4.4: Raman spectra of a typical 5L FeCl₃-FLG device taken at different locations after fabrication (a), after 3 months (b) and after one year (c).

doped graphene taken at the same transmittance. Therefore due to its outstandingly high electrical conductivity and optical transparency FeCl₃-FLGs these materials are the most promising transparent conductors for optoelectronic devices.

In conclusion, we demonstrate novel transparent conductors based on few layer graphene intercalated with ferric chloride with an outstandingly high electrical conductivity and optical transparency. We show that upon intercalation a record low sheet resistance of 8.8 Ω is attained together with an optical transmittance higher than 84% in the visible range. These parameters outperform the best values of ITO and of other carbon-based materials. Another advantage of FeCl₃-FLGs is bendability. It opens perspectives for use of these materials in future flexible electronics. The FeCl₃-FLGs are relatively inexpensive to make and they can be scalable to industrial production of large area electrodes. Contrary to the numerous chemical species that can be intercalated into graphite, many of which are unstable in air, we found that FeCl₃-FLGs are air stable on a timescale of at least one year. Other air stable graphite intercalated compounds can only by synthesized in the presence of Chlorine gas, [30] which is highly toxic. On the contrary, here we demonstrate that the intercalation of FLG with FeCl₃ is easily achieved without the need of using Chlorine gas, which ensures a safe and environmentally friendly industrial processing. Furthermore, the low intercalation temperature (360°C) required in the processing allows the use of a wide range of transparent flexible substrates which are compatible with existing transparent electronic technologies. These technological advantages combined with the unique electro-optical properties found in FeCl₃-FLG make these materials a valuable alternative to ITO in optoelectronics.
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Figure 4.5: Square resistance versus transmittance at 550nm for 4L and 5L FeCl$_3$-FLG (from these experiments), ITO [41] carbon-nanotube films [38] and doped graphene materials [50]. FeCl$_3$-FLG outperform the current limit of transparent conductors, which is indicated by the grey area.
Chapter 5

Current annealing of suspended graphene devices

5.1 Introduction

In this chapter we provide a systematic experimental investigation of the electrical breakdown of suspended mono- to trilayer graphene devices. We show that oxidation of graphene flake at the characteristic temperature of 1400 K is the reason of breakdown in most of our samples. This is caused by the presence of residual oxygen atmosphere around graphene flakes during annealing. At the same time few samples break at temperatures above 2200 K, most probably due to sublimation of carbon atoms. Our results propose a current annealing recipe optimal for reproducible significant improvement of the transport properties of suspended graphene. In the final paragraph we also discuss how the details of the fabrication process can affect post-annealing quality of the sample.

5.2 Current annealing of carbon-based electronic devices

In order to remove the fabrication contaminants from the surface of supported graphene the current-annealing method was proposed [97]. The same method was used for cleaning of suspended mono- and bilayer graphene [18,19,98,99] and trilayer graphene [14]. Before the annealing the suspended graphene is characterised by a high degree of
inhomogeneity causing the so-called electron-hole puddles [76, 100]. The shape of the $R-V_G$ dependence of pre-annealed graphene is irregular (Fig. 5.1) and the width of the neutrality peak is strongly sample-dependent. The resulting mobility of as-fabricated samples ranges between 1000 and 100000 cm$^2$/Vs. This is due to random deposition of dry residue on the surface of the graphene membrane during the final HF-etching step of the fabrication. This residue can be seen in Fig. 3.2.

This surface contamination can also explain the lack of reproducibility of the annealing results. Certain devices initially have little contamination and require a low current to get mobility up to 1,500,000 cm$^2$/Vs [19]. At the same time other devices have large amount of contamination which requires very high current to evaporate the residues, even higher than a certain breakdown value. This critical current value depends on the device geometry and electrical resistivity. The latter question has not been addressed in the literature in detail. Previous experimental papers assume that there is a critical current per unit of cross-sectional area ranging from $(1-2) \cdot 10^8$ A/cm$^2$ in one group of reports [18, 97] to $6 \cdot 10^9$ A/cm$^2$ in others [101]. Some authors consider the current density to be the most important parameter with the critical value ranging from 0.1 mA/µm [99] to (0.5 - 1) mA/µm [19, 98]. The heating power normalised to the area of the flake was also mentioned in the case of annealing of supported samples [97]. It is worth noticing that the influence of annealing time and background temperature was not mentioned in the literature.

As the breakdown critical parameters are not well established, one has to increase the annealing current gradually until the contamination is removed from the graphene surface. This is experimentally realised in the pulse annealing method [18, 19, 98]. Short rectangular current pulses (less than 2 seconds long) are applied to graphene at high vacuum ($10^{-6} - 10^{-7}$ mbar). The background temperature is 4.2 K. After each annealing pulse a low-bias $R(V_G)$ curve can be measured to indicate whether positive changes have occurred. If not, the procedure is repeated with higher current. The first pulse is always chosen to be of deliberately low magnitude. This procedure is repeated until the sample is cleaned to a required level. Sample destruction occurs in most of the cases before transport characteristics are improved. In this thesis we present data obtained using the pulsed annealing technique.

The aims of this chapter are:
Figure 5.1: Effect of current annealing on suspended graphene sample. Before annealing the shape of $R - V_G$ characteristic is irregular (black curve), the neutrality peak is wide. This indicates strong non-uniformity of graphene surface. Current annealing makes the sample uniform (red curve) and increases the mobility.

- to establish the reason of suspended sample breakdown
- to find out the relation between the breakdown current, the sample resistance and geometry
- to suggest an optimised annealing recipe

The picture of a current-broken device is shown in Fig. 5.2. It makes one think that a contact explosion took place and caused the whole device to be not operational. The metal seems to be melted or evaporated possibly due to Joule heating [102, 103], although we should consider also other possibilities, such as:

- electromigration of gold in the graphene-metal interface
- electromigration of carbon atoms
- sublimation of carbon atoms due to Joule heating
The question of breakdown mechanism has been raised previously for other carbon-based devices which utilise carbon nanotubes [104], carbon nanofibers [105, 106], graphene nanoribbons [107], graphene on diamond substrate [108] and Si/SiO$_2$ substrate [109][23]. In these works the question was solved by the method of correlation of the breakdown current and the sample resistance. Namely, one builds a certain model of heat transfer to find dependence of the maximal temperature (normally in the middle of the device) on the Joule heat generated inside graphitic material: $T_{\text{max}} = cI^2R$. The coefficient $c$ depends on the particular model of heat transfer and accounts for the device geometry. Then one assumes that breakdown takes place when the maximal temperature achieves a certain sample-independent limit: $T_{\text{max}} = T_{\text{br}}$. Finally an ensemble of samples with different resistances and geometries is destroyed by electric current so that the breakdown current differs for each sample. The assumption of equal breakdown temperature is correct if the breakdown current $I_{\text{br}}$ correlates with the device parameters in the right way, that is $I_{\text{br}}^2 \propto (cR)^{-1}$. Furthermore, it is possible to extract the breakdown temperature as the fitting parameter to relate it to a certain destruction mechanism. If the correlation $I_{\text{br}}^2 \propto (cR)^{-1}$ does not hold, either the chosen model of heat transfer is incorrect (namely, the functional dependence of the coefficient $c$ on the device dimensions) or the Joule heating is not the cause of the device breakdown (with the electromigration as a possible alternative).

In the experiments [10],[16-18],[20],[23] the reason for device failure was carbon oxidation in ambient atmosphere when local temperature reaches 600°C. To identify
the reason for the breakdown of our devices we consider three models of heat transfer:

1. **1D model for the temperature profile of metallic contact.** This model is valid for narrow contacts and will be used to verify the hypotheses that a suspended graphene device is destroyed due to melting or evaporation of the contacts at a certain critical temperature.

2. **2D model for the temperature profile of metallic contact.** This model is valid for wide contacts. Together with the 1D model above, it will be used to verify the hypotheses that a suspended graphene device is destroyed due to melting or evaporation of the contacts at a certain critical temperature.

3. **1D model for the temperature profile of graphene flake.** This model will be used to verify the hypothesis that a suspended graphene device is destroyed due to graphene oxidation or sublimation at a certain temperature in the middle of the flake.

These models are examined in details in the next section.

### 5.3 Models of heat transfer for suspended graphene

#### 5.3.1 1D model for the temperature profile of a metallic contact.

![Diagram of 1D heat transfer model for a metallic contact](image)

Figure 5.3: Illustration of the 1D heat transfer model for a metallic contact. The flake on the left side injects heat flux into the contact. The flux diminishes along the contact due to thermal leak into the substrate. Temperature gradient in silicon is negligible.

We begin with a simple 1D model of heat flow to find the highest temperature in metallic contact. The schematic of the contact is given in Fig. 5.3. This model is valid when the temperature drop in the $y$ direction is much less than in the $x$ direction. Consequently there is no heat flow to the sides of the contact. We also neglect the
temperature variation along the $z$ axis due to small thickness of contact $h_c$. The temperature of the metal depends only on one coordinate: $T = T(x)$. $T(x)$ has its maximum at the point where the heat flux $I^2R/2$ is injected, i.e., at the contact with the flake ($x = 0$).

According to the Fourier’s law the heat flux density is:

$$q = -\kappa_{Me} \frac{dT}{ dx},$$  \hspace{1cm} (5.1)

where $\kappa_{Me}$ is the metal thermal conductivity. The total heat flux through the metal is equal to

$$Q = qS = qW_c h_c,$$  \hspace{1cm} (5.2)

where $W_c$ is the contact width. Due to heat leak into the substrate (heat flux density is $q_{\text{leak}}$) the heat flux will decrease with increase of coordinate $x + dx$:

$$dQ = -q_{\text{leak}} W_c dx = -\alpha (T - T_\infty) W_c dx.$$  \hspace{1cm} (5.3)

Here the leakage $q_{\text{leak}} = \alpha (T - T_\infty)$ with the heat transfer coefficient $\alpha = \kappa_{SiO_2}/h_{SiO_2}$ [103]. This assumption is based on the high thermal conductivity (approximately 150 W/(mK) [104]) and large thickness of silicon compared to the corresponding parameters of SiO$_2$ layer. This causes very effective temperature equalising inside silicon. Irrespective of the position the silicon temperature can be taken equal to the background temperature $T_\infty$. The small thickness of SiO$_2$ compared to the characteristic spatial scale of temperature profile of the contacts is also required for the validity of the assumption $q_{\text{leak}} = \alpha (T - T_\infty)$. Otherwise the leakage will depend not only on the local temperature of the contact, as it is illustrated in the Fig. 5.4. The condition of small thickness of SiO$_2$ will be checked later when the solution for the temperature profile will be obtained.

Taking into account Eq.(5.1) and Eq.(5.2) and introducing the new variable $T - T_\infty = \Theta$ we can rewrite Eq.(5.3) as

$$\frac{\kappa_{Me} h_c}{\alpha} \frac{d\Theta}{ dx} = \Theta dx.$$  \hspace{1cm} (5.4)

Following ref. [104] we introduce the so-called healing length $L_H = \sqrt{\kappa_{Me} h_c/\alpha}$ =
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Figure 5.4: a) The characteristic spatial scale \( L_H \) of the contact temperature profile is much greater than the dielectric thickness \( h_{SiO_2} \). In this case heat flux lines in the dielectric are perpendicular to the substrate surface. The value of the leakage heat flux at a certain coordinate \( x \) depends only on the local temperature of the contact. b) \( L_H \) is comparable with \( h_{SiO_2} \). The heat flux lines in the dielectric have significant horizontal components. The value of the leakage heat flux at a certain coordinate \( x \) has a complicated dependence on the temperature of the adjacent areas.

\[
\sqrt{h_c h_{SiO_2} \kappa_{Me} / \kappa_{SiO_2}}. \quad \text{In terms of } L_H \text{ the heat equation becomes } L_H^2 \Theta'' = \Theta. \quad \text{Its solution is the sum of two exponential functions } \Theta = \Theta_m e^{-x/L_H} + \Xi e^{x/L_H}. \quad \text{We have to satisfy 2 boundary conditions. The first one is } T(\infty) = T_\infty, \text{ or } \theta(\infty) = 0. \quad \text{It sets } \Xi = 0 \text{ to suppress the term with the exponential temperature growth. The second boundary condition is } Q(0) = I^2 R/2. \quad \text{Taking into account (5.1) and (5.2) the second boundary condition gives}
\]

\[
k_M \frac{\Theta_m}{\Theta_H} W_c h_c = \frac{I^2 R}{2 L_H} = \frac{I^2 R}{2 L_H} \frac{L_H}{2 \kappa_{Me} w_c h_c}.
\]

Finally, we get the solution

\[
\Theta = \frac{I^2 R L_H}{2 \kappa_{Me} w_c h_c} e^{-x/L_H}.
\]

The temperature is maximal at the point where flake is connected to the contact: \( \Theta_{max} = \Theta|_{x=0} = \Theta_m \). If we introduce \( R_1 = R/W_c \) we can rewrite \( \Theta_m = \frac{I^2 R_1}{2 \kappa_{Me} w_c h_c} \). The value of the fraction \( \frac{L_H}{2 \kappa_{Me} w_c h_c} \) is equal for all our devices. Then we can conclude that if the suspended devices are broken due to contact damage at a certain sample-independent temperature \( \Theta_{br} \), the breakdown current should satisfy the relation \( I^2 \propto R_1^{-1} \).

Once we know the characteristic spatial scale of temperature profile \( L_H \) we can
compare it to the characteristic width of metallic contacts used in our experiments $W_c = 7 \ \mu m$ and the thickness of silicon dioxide layer $h_{SiO_2} = 0.3 \ \mu m$. To find the healing length we take the height of contacts used in our experiments $h_c = 0.09 \ \mu m$, thermal conductivity of gold $\kappa_{Me} = 450 \ W/(mK)$ and thermally oxidised SiO$_2$ $\kappa_{SiO_2} = 1\ W/(mK)$ [111]. The resulting healing length is 3.1 $\mu m$ and is comparable to the characteristic temperature relaxation length reported before for similar conditions (Fig.4b in the supplementary material of [111]).

As we can see the healing length is an order of magnitude larger than the thickness of the dielectric. This validates the model of heat leakage $q_{\text{leak}} = \alpha(T - T_\infty)$. On the other hand the healing length is comparable to the typical width of the contact. This means that the 1D model cannot explain heat flow along the $y$ direction.

![Figure 5.5](image_url)

Figure 5.5: Illustration to the two-dimensional heat transfer model for metallic contact (top view).

### 5.3.2 2D model for the temperature profile of metallic contact.

Now we proceed to develop the two-dimensional model for the temperature profile of metallic contact. We will assume $W_c > L_H \gg W$, where $W$ is the flake width. This assumption is opposite to the model above where $L_H \gg W, W_c$. Both cases are approximations to the real situation $W_c \sim L_H > W$, for which there is no analytical
solution. The exact solution of the problem should also take into account the non-trivial geometry of the interface between metal and graphene (notice that that part of metal contact which covers graphene flake does not have SiO$_2$ underneath due to HF-etching. Consequently there is no thermal coupling to the substrate in that region).

In the model under consideration heat flows in radial direction outside the region of the radius $W/2$ (Fig. 5.5) and temperature is the function of radius: $T = T(r)$. Inside this region the lines of heat flux turn to become perpendicular to the metal edge. The model does not consider the temperature field inside this region but enables one to find the temperature on the radius $W/2$. If $L_H \gg W$ this temperature will be close to the maximal temperature of the metallic contact. To find the temperature outside we start with the Fourier’s law:

$$q = -\kappa_{Me} \frac{dT}{dr}. \quad (5.6)$$

The total heat flux through a ring of radius $r$ is equal to

$$Q = qS = q2\pi rh_c. \quad (5.7)$$

Due to the heat leak to SiO$_2$ the heat flux will be different at the next ring $r + dr$:

$$dQ = -q_{\text{leak}}dS_{\text{ring}} = -q_{\text{leak}}2\pi rdr = -\alpha(T - T_\infty)2\pi rdr.$$

Here $dS_{\text{ring}}$ is the area enclosed between two rings. Taking into account Eq.( 5.6) and Eq.( 5.7)

$$d(-\kappa_{Me} \frac{dT}{dr}2\pi rh_c) = -\alpha(T - T_\infty)2\pi rdr,$$

$$d(\kappa_{Me} \frac{d\Theta}{dr}rh_c) = \alpha\Theta rdr, \quad (T - T_\infty = \Theta)$$

$$\frac{\kappa_{Me}h_c}{\alpha}d(\frac{d\Theta}{dr}r) = \Theta rdr.$$

Let us use the formula for the healing length $L_H = \sqrt{\kappa_{Me}h_c/\alpha}$:
After introducing the new independent variable \( x = r/L_H \) the heat equation becomes:

\[
\frac{d}{dx} \left( \frac{d \Theta}{dx} x \right) = \Theta x,
\]

\[
x^2 \Theta'' + x \Theta' - (x^2 + 0^2) \Theta = 0.
\]

This is the modified Bessel’s equation, and its solution is expressed by the modified Bessel’s functions of 0-th order: \( \Theta = C_1 I_0(x) + C_2 K_0(x) \). We have to satisfy 2 boundary conditions. The first one is \( T(\infty) = T_\infty \) or \( \Theta(\infty) = 0 \). This sets \( C_1 = 0 \) and \( \Theta = C_2 K_0(x) \) as the function \( I_0 \) is unlimited at the infinity while \( K_0(x) \) approaches 0. The second boundary condition is \( Q(W/2) = I^2 R \). Rewriting Eq. (5.6) as \( q = -\kappa Me C_2 dK_0/L_H dx \) and substitution to the second boundary condition gives

\[
-\kappa Me \frac{C_2 dK_0(W/2L_H)}{L_H dx} 2\pi \frac{W}{2} h_c = I^2 R.
\]

Taking into account the following property of the modified Bessels functions: \( dK_0/dx = -K_1 \), we finally can define the coefficient \( C_2 \) and the final solution:

\[
\Theta(r) = \frac{I^2 RL_H}{\pi Wh_c \kappa Me} K_0(r/L_H) K_1(W/2L_H).
\]

The temperature is highest at the radius \( r = W/2 \) closest to the flake

\[
\Theta_{max} = \frac{I^2 RL_H}{\pi Wh_c \kappa Me} K_0(W/2L_H) K_1(W/2L_H).
\]

Then, by introducing the new notation

\[
R_2 = \frac{R}{W} \frac{K_0(W/2L_H)}{K_1(W/2L_H)},
\]

we can express the maximal temperature as \( \Theta_m = I^2 R_1 \frac{L_H}{\pi \kappa Me h_c} \). If our suspended
devices are broken due to contact damage at certain temperature $\Theta_{br}$, the breakdown current should then satisfy $I_{br}^2 \propto R^{-1}$. The coefficient of proportionality depends on the breakdown temperature and can be found as a fitting parameter.

5.3.3 Temperature profile in the flake

![Flake temperature profile diagram](image)

Figure 5.6: Schematic of the flake temperature profile. The contact temperature is the boundary condition at $x = L/2$ for the heat equation defining flake temperature profile.

As we deal with the suspended graphene there is no direct heat leak from the flake to the substrate. Instead, heat is produced by the Joule heating. For simplicity we assume the energy to be released uniformly within the flake. Then it flows to the metallic contacts. It is natural to choose a one-dimensional model for the heat flow as there is no heat flux to the sides of the flake and all the flux lines are directed towards the contacts (then the model is identical to the one used in Ref. [106] for the problem of heating in suspended carbon nanofibers). Taking into account that the maximal temperature of the flake is in its middle it is convenient to choose the origin of the problem at the middle (Fig. 5.6). We begin with the Fourier’s law:

$$ q = \kappa \frac{dT}{dx}. \quad (5.10) $$

The total heat flux through the flake is equal to $Q = qS = qWh_1N_L$

$$ Q = qS = qWh_1N_L. \quad (5.11) $$
where \( h_1 \) is the thickness of monolayer, \( N_L \) is the number of layers. Due to heat generation (amount generated on the length \( dx \) is \( I^2Rdx/L \)) the heat flux will increase with the increase of coordinate \( x + dx \): \( dQ = I^2Rdx/L \), or, taking into account (5.10) and (5.11):

\[
d(-\kappa \frac{dT}{dx} Wh_1 N_L) = I^2Rdx/L.
\]

For sake of clarity let us count the temperature with respect to the temperature of contacts: \( T - T_c = \Theta \), where \( T_c \) is the temperature on the contacts. Then from Eq. (5.12) \( \Theta'' = -A \), where \( A = \frac{I^2R}{\kappa WLh_1N_L} \). The integration of this equation gives \( \Theta = c + bx - Ax^2/2 \). We will use two boundary conditions to find the coefficients \( c \) and \( b \). The first boundary condition accounts for the fact that temperature is a symmetric function and has its maximum in the middle of the flake. This sets the coefficient \( b = 0 \). According to the second boundary condition, \( \Theta(L/2) = c - AL^2/8 = 0 \). Taking this into account we obtain the temperature profile \( \Theta(x) = \frac{I^2R}{2\kappaWLh_1N_L}(L^2/4 - x^2) \). The maximal temperature in the middle is

\[
\Theta_{\text{max}} = AL^2/8 = \frac{I^2RL^2}{8\kappa WLh_1N_L} = \frac{I^2RN_{sq}}{8\kappa h_1N_L}.
\]

We should take into account that thermal conductivities of mono- bi- and trilayer graphene are different [112]. For convenience of fitting let us normalise these to the thermal conductivity of monolayer graphene \( k_1 \):

\[
\Theta_{\text{max}} = \frac{I^2}{8\kappa_1h_1} \frac{R N_{sq}}{N_L} \frac{\kappa_1}{\kappa} = \frac{I^2}{8\kappa_1h_1} R_3.
\]

At room temperature \( \kappa_1/\kappa = 1.43 \) for suspended bilayers and \( \kappa_1/\kappa = 1.77 \) for suspended trilayer graphene [112]. Introducing new notation \( R_3 = R\kappa_1N_{sq}/(\kappa N_L) \) we can say that if our suspended devices are broken due to flake damage at certain temperature \( \Theta_{br} \), then the breakdown current should satisfy the relation \( I_{br}^2 \propto R_3^{-1} \).

A summary of three models discussed in this section is given in Tab. 5.1
Table 5.1: Summary of heat transfer models

<table>
<thead>
<tr>
<th>Model</th>
<th>Validity</th>
<th>Maximal temperature</th>
<th>Breakdown current</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contacts 1D</td>
<td>$L_H \gg W, W_c$</td>
<td>$\Theta_{\text{max}} = \frac{I^2 RL_H}{2 \kappa_M w_c h_e}$</td>
<td>$I_{br}^2 \propto R_1^{-1}$, $R_1 = \frac{R}{W}$</td>
</tr>
<tr>
<td>Contacts 2D</td>
<td>$W_c &gt; L_H \gg W$</td>
<td>$\Theta_{\text{max}} = \frac{I^2 RL_H}{\pi w_c \kappa_M K_0(W/2L_H)}$</td>
<td>$I_{br}^2 \propto R_2^{-1}$, $R_2 = \frac{R K_0(W/2L_H)}{W K_1(W/2L_H)}$</td>
</tr>
<tr>
<td>Flake 1D</td>
<td>$\kappa_1 = \text{const}$</td>
<td>$\Theta_{\text{max}} = \frac{I^2 R N_{sq}}{8 \kappa_1 N_L}$</td>
<td>$I_{br}^2 \propto R_3^{-1}$, $R_3 = R_3^{\kappa_1 N_{sq}} N_L$</td>
</tr>
</tbody>
</table>

5.4 Experimental results

In order to examine the mechanism of the devices failure at a certain temperature of contacts or flake we have performed current annealing of 21 samples of different thicknesses (mono- to trilayer) and different geometries (See the table in Appendix A). We measured the resistance during the annealing process. Then we calculate $R_1$, $R_2$ and $R_3$ for each flake and plot them against the square of the breakdown current in the logarithmic scale (Fig.5.7 to Fig.5.9). This is followed by linear fits, with the slope of fit corresponding to the power in the dependence $I_{br}^B \propto R_i^{-1}$ ($i = 1 - 3$) and intercept determining the characteristic temperature.
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Figure 5.7: Correlation between breakdown current and breakdown resistance normalised to the contact width $R_1 = R/W$. The line is the best fit to the dependence $I_B \propto R_1^{-1}$. The contact temperature is extracted from the equation (5.4).

Figure 5.8: Correlation between breakdown current and breakdown resistance normalised to the flake width according $R_2 = \frac{R}{W} \frac{K_0(W/2L_H)}{K_1(W/2L_H)}$. The line is the best fit to the dependence $I_B \propto R_2^{-1}$. The contact temperature is extracted from the equation (5.8).

The comparison of the annealing data with the models describing temperature of the contacts shows that there is a correlation between breakdown current and flake...
resistance (Fig.5.7 and Fig.5.8). The coefficients of determination $R^2$ (See, for example [113]) are 0.76 for the one-dimensional model and 0.79 for the two-dimensional model. Let us focus on the later model.

Figure 5.9: Correlation between breakdown current and sample resistance normalised according to $R_3 = R_{\kappa_1} N_{sq}/(\kappa N_L)$. The line is the best fit to the dependence $I_{br}^{B_0} \propto R_3^{-1}$. The maximal flake temperature is extracted from the equation (5.13).

Relatively high $R^2$ means that there is a good correlation between $I_{br}$ and $R_2$. According to the intercept of the fit the characteristic contact temperature temperature $T_c$ at the event of breakdown is 75K. Although there is a significant fitting error of 45 K. Even greater error is caused by the power of the dependence $I_{br}^{B_0} \propto R_3^{-1}$ being $B = 1.6$ which is considerably different from two. This indicates that the devices with low $R_2$ have higher temperature (approximately 150 K) than the devices with high $R_2$. Taking into account the physical meaning of $R_2$ (See (5.9)), this implies that the wider the flake is, the higher is the temperature of the contact at the breakdown event. This will be discussed later at the end of the paragraph when the physical reason of the breakdown will be clear. Now we can conclude that the characteristic temperature of the contacts is not higher than 200 K in our experimental conditions. At this low temperature neither metal melting nor any other contact destruction is possible. The
same reasoning arises when we consider the 1D model of contact temperature.

Now we compare the experimental data with the 1D model of the flake temperature. Fig.5.9 demonstrates correlation between current and the resistance with the correct power $B = 2.07$. In order to find the flake temperature as a fitting parameter we have to substitute into the formula Eq.(5.13) the monolayer graphene thermal conductivity as a temperature-independent parameter. However it is known that thermal conductivity decreases with temperature due to umklapp process both for monolayer and few-layer graphene [111, 114]. In case of monolayer it falls from $4400 \text{ W/(mK)}$ at room temperature (when it is close to the maximum) to $600 \text{ W/(mK)}$ at $1100 \text{ K}$. Within this work we take an arithmetic mean of $2500 \text{ W/(mK)}$ and substitute it in Eq.(5.13). There is no way of choosing a correct mean thermal conductivity because of the complicated non-linear dependence $\kappa_1(T)$ and non-linear temperature profile $T(x)$. The correct solution would be incorporating the temperature dependence into Eq.(5.12) and numerical calculation. In this case we would not be able to have an analytical formula for statistical analysis.

The result of fitting using the model (5.13) is the average breakdown temperature $\Theta = 1150 \text{ K}$. The coefficient of determination $R^2$ for this fit is 0.73. There can be several reasons for the observed scatter of experimental points. The first one is the discussed temperature dependence of graphene thermal conductivity. The other reason is the annealing conditions which may be in some way different for different samples. We find this reason to be the main source of the scatter and will discuss it in details later in the paragraph 5.5. Also non-uniform heat generation inside the flake is possible due to nonhomogeneous flake resistivity. Finally, the fit in Fig.5.9 represents not the actual temperature in the middle of the flake but the temperature with respect to the contacts, where, in accordance with Fig.5.8, temperature is of the order of $100 \text{ K}$.

Fig.5.10 illustrates this idea for the example of two devices destroyed at the same absolute temperature in the middle of the flake. One of the devices has higher $R_3$. We will call this device the ”narrow” one. The other, ”wide” device has lower $R_3$. Practically the higher $R_3$ could be due to higher resistance, longer, narrower or thinner flakes. According to equation (5.13) the ”wide” device will have a lower relative temperature $\Theta$ than the ”narrow” one. This will introduce the additional scatter for the data points in Fig.5.8 and Fig.5.9 even if the absolute temperature of the flake is the same in the middle of the flakes. Another source of error would be increased temperature of the
contacts at the event of device breakdown for the "wide" flake. This is manifested by
the decreased power of \( B = 1.6 \) in the dependence \( I_{br}^2 \propto R_i^{-1} \) in Fig.5.8.

Figure 5.10: Two samples with equal absolute temperature in the middle have slightly
different flake temperatures relative to the contacts.

In order to eliminate the source of error mentioned above and to correct for the
failure temperature of few-layer graphene flakes we should deal with the absolute flake
temperature. For this purpose let us sum up the temperatures (5.8) and (5.13):

\[
T_{\text{max}} = T_{c\text{max}} + \Theta_{f\text{max}} = \frac{I^2RLH}{\pi \kappa_0(W/2LH)} K_0(W/2LH) + \frac{I^2}{8\kappa_1h_1} R_3,
\]

(5.14)

\[
T_{\text{max}} = \frac{I^2R}{8\kappa_1h_1} \left( \frac{h_1}{\kappa_0 \kappa_{Me}} \frac{LH}{W} \frac{8}{\pi} K_0(W/2LH) + \frac{N_{sq} \kappa_1}{N_L \kappa} \right),
\]

With the definition of \( R_4 = R(\frac{h_1}{\kappa_0 \kappa_{Me}} \frac{LH}{W} \frac{8}{\pi} K_0(W/2LH) + \frac{N_{sq} \kappa_1}{N_L \kappa}) \) the expression for \( T_{\text{max}} \) becomes

\[
T_{\text{max}} = \frac{I^2}{8\kappa_1h_1} R_4,
\]

(5.15)

In order to show that our suspended devices fail due to flake damage at certain
temperature \( T_{br} \) we have to check the dependence \( I_{br}^2 \propto R_i^{-1} \). The interpretation of
our experimental data corresponding to this hypothesis is shown in Fig.5.11. The fit is insignificantly improved compared to that in Fig.5.9: The power is equal 2 ± 0.25 (compared to 2.07 ± 0.27 in Fig.5.9), the coefficient of determination \( R_2 \) is 0.76 (compared to 0.73). The absolute temperature extracted from the intercept of the fit
is 1340 ± 70 K and is reasonably high for destring the graphene. The mechanism of
device failure may be either sublimation or oxidation and will be discussed in the next
Before we proceed we should exclude any kind of electromigration from our consideration. If electromigration were the cause for the failure we would observe a certain sample-independent breakdown current density. In contrast, our data show breakdown current densities ranging from 0.73 mA/µm to 2.77 mA/µm (or from $1.1 \cdot 10^8$ A/cm$^2$ to $4.1 \cdot 10^8$ A/cm$^2$). Moreover, it was reported that graphene on diamond can withstand currents higher than $18 \cdot 10^8$ A/cm$^2$ without suffering from electromigration at the temperature of approximately 1000 K [108]. The graphene transistors used in that study were destroyed due to oxidation caused by Joule heating. Thanks to diamond substrate which acts as a heat sink the characteristic current is higher than that demonstrated in our work.

Electromigration-caused graphene breakdown was reported before at the current densities about 2 mA/µm in [115, 116], where the authors demonstrate graphene-based atomic-scale switches and focus on the study of their operation. The on/off behaviour of the destroyed flakes is used as the evidence of the electromigration breakdown.
However in our opinion the electromigration can be a final step of sample destruction, when a thermal process like sublimation or oxidation serves as trigger. In this case critical parameters are defined by the trigger process. After the process is initiated the width at the middle cross-section decreases and the current density at this section diverges. Neither exact breakdown current nor its statistical correlation to the sample resistance is given in ref. [115,116]. Therefore, like in ref. [108], we incline to conclude that carbon electromigration is not the reason for the failure of suspended devices.

The idea that oxidation or sublimation triggers the breakdown which is then finished via another mechanism helps us to understand the picture of our typical broken device (Fig.5.2). This photograph suggests major heat loaded to the contacts rather than to the flake which contradicts the characteristic contact temperature of less than 200 K found in this work. The heat caused contact melting could be released at the final phase of the breakdown when there is either a very narrow constriction or the flake is significantly disordered and has large ohmic resistivity. Electromigration of gold also cannot explain the device failure. Taken into account the thickness of the contacts, the current density there is less than $4 \cdot 10^6 \text{ A/cm}^2$ which is much less than limit of $10^8 \text{ A/cm}^2$ [103].

5.5 Discussion

In this section we will discuss the mechanism of the failure of graphene devices, the influence of annealing conditions and evolution of graphene transport quality during the annealing process. The optimised annealing recipe will be given.

As we have seen in the previous section graphene sublimation or oxidation is the reason of electrical breakdown of a suspended graphene device. In order to distinguish between these two mechanisms we have, first, to establish the characteristic temperature of graphene sublimation and, second, find possible source of oxygen or water in the atmosphere around the flake.

There are numerous publications concerning graphite sublimation. According to [117] it would lose $10^{-5}$ gram from a surface of 1 m$^2$ per second at the temperature of 2200 K. In terms of a single graphitic plane, it means that 2.5% of carbon atoms will evaporate from the outer layer of graphite per 1 second. In other words, the characteristic time of evaporation of monolayer of carbon atoms from a graphitic surface
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is 40 seconds. At the temperature of 2800 K this will take 0.01 seconds. We can assume the same sublimation rate for monolayer graphene and few-layer graphene. This is reasonable because the sublimation process is due to breaking of $\sigma$-bonds which have essentially the same energy for graphene and graphite. Due to evaporation from both top and bottom sides of the flake we can say that it takes approximately 20 seconds to sublime monolayer graphene at 2200 K and 0.005 seconds at 2800 K. As we perform annealing using short pulses of approximately 2 seconds long, we can say that a flake can survive after one or two current pulses if they heat the middle of the flake to 2200 K, although the flake will be disordered and its electron mobility will decrease. So we will consider this temperature to be the lowest temperature before we damage the flake. Although we cannot concede that a flake will survive if heated to 2800 K. Therefore the interval between these two temperatures is the dead zone from the point of view of sublimation. This is supported by the fact that multi walled carbon nanotubes sublime at the temperature of 2800 K [118]. At the same time, suspended graphene was recently reported to be kept at 2000 K in vacuum for sufficient time without any damage [101,119–121].

Now we can draw two lines in Fig.5.11 corresponding to the deadzone. We can see that 4 out of 21 devices are probably destroyed by flake sublimation.

The breakdown temperature of the rest of the two third of our devices is also quite high, although not enough for sublimation. We have to conclude that the most probable mechanism of failure of these samples is graphene oxidation at the middle of the flake. The oxidation temperature of graphene and carbon nanotubes in ambient atmosphere is approximately 800 K [97,104,107]. In oxygen-depleted dry nitrogen atmosphere this temperature is elevated up to 1050 K with the oxygen sourced presumably from the SiO$_2$ substrate [111]. In our experiments all the annealing sessions were performed at high vacuum (the pressure of approximately $10^{-6}$ mbar). The background temperature is 4.2 K to assure that the outgassing rate is low and all the contamination that has been removed from graphene surface is trapped by the substrate. Nevertheless there is always a source of residual water and oxygen atmosphere [122,123]. Its density may become locally increased during the annealing by outgassing from the regions of SiO$_2$ which are adjacent to the relatively hot metallic contacts (red area in the Fig.5.3). This outgassing may source not only oxygen but also water which is always absorbed by the surface of SiO$_2$ etched by the HF acid [124].
Nevertheless for most of our samples oxidation occurs at significantly higher temperatures than 1050 K. In our experiments graphene is not in direct contact with the substrate thanks to the flakes being suspended. This restricts the oxidation mechanism. The local residual atmosphere during annealing is not a controlled parameter in our experiments. Therefore we observe the oxidation temperature ranging between 700 K and 2200 K. This is the main source of the above-mentioned fitting error in Fig.5.11. The breakdown temperature can be elevated up to the sublimation limit of 2200 K when presence of SiO$_2$ is eliminated [119,120], or if graphene is suspended over Si/SiN platform [121]. In the articles mentioned above suspended samples could stand temperatures as high as 2000 K.

Now let us track the evolution of graphene transport characteristics during the annealing process. After each annealing pulse we perform a standard low-bias $R - V_G$ measurements to monitor mobility and the neutrality point evolution. We have noticed that as the flake temperature approaches the average breakdown limit the sample characteristics degrade (See Fig.5.12): the neutrality peak shifts in random direction and broadens indicating disordering. In other words, the doping of the sample becomes non-uniform and the resistance of the sample is less modulated by the gate voltage. In the case of monolayer samples this means that high temperature causes introduction of point defects (resistance is dominated by short-range scattering). The sample degradation evolves with time if the annealing is repeated with the same current. This observation supports the idea that the whole device fails due to gradual flake destruction. Several examples of annealing paths are shown in Fig.5.13. The red segment of a polyline denotes an annealing step where irreversible degradation of transport characteristics was observed.

At the annealing steps preceding flake destruction (blue part of an annealing path) we have noticed two different types of resistance evolution. The first type is characteristic for most of the samples and implies no changes irrespective of duration of annealing. Another type of sample evolution is a positive change (Fig.5.14). Once we have seen an improvement at a certain current no further improvement was observed at the same current irrespective of annealing duration.

This diverse behaviour of various samples points to an arbitrary placement of fabrication contamination on samples. Some samples occasionally have little contamination which does not require too high temperature for evaporation. Other samples have hard
contaminants which have no chance to be removed even at temperatures which destroy graphene structure via oxidation or sublimation. The insignificance of annealing time for positive changes in $R - V_G$ characteristics points to the importance to reach a certain temperature to remove certain contaminants. In other words, the characteristic time of temperature relaxation in the system is much less than a characteristic duration of the annealing pulse. If some contaminants were not removed during a one second-long annealing then the temperature is not enough for this contaminants and long exposition time does not improve the sample. The characteristic temperature relaxation time is easy to estimate (See Appendix B). The steady state temperature profile stabilises in microseconds. As we can see, annealing step of 1 second duration is long enough to heat the flake and all the contaminants to a target temperature.

5.6 Conclusions

In conclusion, we show that current-induced breakdown of a suspended graphene or few-layer graphene devices is initiated by oxidation and sublimation of graphene. Electromigration or contact melting can be a final stage of this process. A simple relationship between the maximum annealing current, sample resistance and geometry is
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Figure 5.13: Sequences of annealing steps for different samples. Blue points represent annealing with positive or no change of sample quality. Red points correspond to sample degradation which occurs when the flake temperature approaches its critical value (brown line). The degradation is followed by the flake destruction.

obtained. These results are an important step for understanding the reliability of the suspended devices for potential applications. Having in mind the conclusions made above we suggest the following annealing recipe:

1. Measurement of the low-bias sample resistance for calculating the maximal safe current at that resistance, according to (5.15)

2. 1 second long annealing pulse at the current equal half of the maximal safe current for measurement of the high-bias resistance

3. Re-calculating maximal safe current taking account of the high-bias resistance

4. 1 second long annealing pulse at the new maximal safe current

5. Analysis of the progress of the high-bias resistance during annealing. If the resistance of the sample decreased significantly during the annealing, it is possible to repeat the procedure with a larger current
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Figure 5.14: An example of sample improvement by current annealing. $R - V_G$ curve becomes narrow, resistance decreases and the neutrality peak shifts to zero.

The annealing following this recipe is quick. A sample is not exposed to high temperature for long time (to avoid accumulative effect of oxidation or sublimation) however it is enough to evaporate all contaminants possible for a given device. If the sample did not improve, its cleaning would imply heating to the higher temperature which can either destroy or disorder the sample. The use of equation (5.15) for estimation of maximal safe current requires knowledge of maximal safe temperature. In case of our devices it can be taken approximately 1000 K. Although this temperature is sample-dependent and therefore can be higher. Understanding the annealing process opens possible routes for further improvement of the quality of suspended-current annealed samples. These routes are essentially elevation of the breakdown temperature towards the sublimation limit and decrease of the melting/evaporation temperature of the fabrication contaminants. The first route can be implemented, for example, by

- in-situ sample drying before the current annealing. Exposure to vacuum at a moderate elevated temperature (400 K) will assist the substrate to degas residual water and oxygen from the SiO$_2$ substrate
- use of an oxygen-free substrate dielectric, for example Si$_3$N$_4$

The second route can be realised by improvement of the fabrication technique, for example use of different etchants and solvents. Ascertaining the chemical composition of the fabrication contaminants is the necessary step to find the characteristic temperatures at which they can melt and evaporate from the graphene surface.
In this thesis the properties of graphene and its few-layers are engineered to make them highly conductive. Two different approaches were implemented to achieve this goal. One approach was to increase the concentration of charge carriers by intercalation of acceptor FeCl$_3$ molecules. Another approach was to increase the mobility of carriers by means of removing surface contamination in the current annealing process.

First, the structure of FeCl$_3$-intercalated few-layer graphene was studied using Raman spectroscopy. It was shown that FeCl$_3$ penetrates between graphene planes and decouples them electrically. Hall measurements and analysis of Shubnikov-de Haas oscillations were used to confirm these findings and to show that FeCl$_3$ molecules accept large electric charge of $\sim 10^{14}$ cm$^{-2}$ per graphene plane.

Second, it was demonstrated that this doping (causes) FeCl$_3$-intercalated few-layer graphene to be an excellent conductor of electricity which is as transparent as pristine graphene. Combination of low sheet resistance and transparency (85% when the sheet resistance is 8.8 $\Omega$), stability in air and bendability makes this material the best transparent conductor among carbon-based materials.

Furthermore, we have conducted a systematic study of the mechanism of electrical breakdown during current annealing of graphene and its few-layers. It was found that the mechanism is either oxidation at the temperature $\sim$1400 K or sublimation of carbon atoms at $\sim$2200 K, depending on the experimental conditions. On the basis of these results the optimised annealing recipe was proposed to avoid the electrical breakdown during the annealing of future suspended devices and to make current annealing a more efficient and reliable method of graphene engineering.
Appendix A

Statistics of the current-broken suspended graphene samples

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Number of layers</th>
<th>$L$ (µm)</th>
<th>$W$ (µm)</th>
<th>$W_c$ (µm)</th>
<th>$I_{br}$ (mA)</th>
<th>$R_{br}$ (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D12S1Q3F1R</td>
<td>2</td>
<td>1.08</td>
<td>1</td>
<td>6.2</td>
<td>1.63</td>
<td>3.58</td>
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<td>1.65</td>
<td>4.1</td>
<td>9</td>
<td>5.12</td>
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<td>6</td>
<td>2.34</td>
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<td>1</td>
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Appendix B

Characteristic temperature relaxation time

According to the equation (5.14) there are two contributions to the flake temperature. One is the contact temperature which requires a characteristic time $\tau_1$ to set in and the other is the temperature profile inside the flake with the characteristic relaxation time $\tau_2$. In order to find the characteristic relaxation time for an unsteady heat transfer process one has to know the Biot number of the problem [125]:

$$Bi = \frac{\alpha L_{scale}}{\kappa} \sim \frac{\Delta T_{in}}{\Delta T_{out}}.$$

Here $\alpha$ is the heat-transfer coefficient for the heat exchange between the body under consideration and surrounding media, $L_{scale}$ is the characteristic spatial scale of the body and $\kappa$ is its thermal conductivity. The physical meaning of the Biot number is the ratio of the internal temperature drop to the temperature difference between the body surface and media. The first formula is more convenient for calculation of $\tau_1$ and the second one - for $\tau_2$:

$$Bi_1 = \frac{\alpha L_H}{\kappa_{Me}} = \frac{\kappa_{SiO_2} L_H}{\kappa_{Me} d_{SiO_2}} = \frac{1W/(K\cdot m)}{450W/(K\cdot m)} \times \frac{3.1\mu m}{0.3\mu m} = 0.023 \ll 1,$$

$$Bi_2 = \frac{\Theta_{f_{max}}}{T_{c_{max}}} \sim \frac{1100K}{100 K} \sim 10 \gg 1.$$

Metallic contact appeared to be a thermally thin body when graphene flake is thermally thick. According to [125] for these cases the characteristic relaxation times can be found from:
Appendix B: Characteristic temperature relaxation time

\[
Bi_1 \frac{\tau_1}{L^2_H \rho_M \kappa_M c_M} \sim 1 \quad \text{and} \quad \frac{\tau_2}{L^2 \rho_G c_G} \sim 1.
\]

Here \(\rho_M\) and \(\rho_G\) are metal and graphene densities and \(c_M\) and \(c_G\) are their specific heat capacities. Substituting the values \(\rho_M = 19.3 \text{kg/m}^3\), \(\rho_G = 2.1 \text{kg/m}^3\), \(C_M = 130 \text{J/(kg·K)}\), \(C_G = 700 \text{J/(kg·K)}\) we obtain:

\[
\tau_1 \sim 10^{-6} \text{sec} \quad \text{and} \quad \tau_2 \sim 10^{-9} \text{sec}.
\]
Bibliography


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