Spintronics and thermoelectrics in exfoliated and epitaxial graphene

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Chapter 1

Introduction and outline

Some sticky tape and a piece of graphite, these were the ingredients used by Andre Geim and Konstantin Novoselov to start a whole new subfield of condensed matter physics, only a bit more than a decade ago. This was the field of two-dimensional materials. The Nobel laureates used their tape to exfoliate (cleave) from graphite a 2D carbon sheet called graphene. It was the first member of a new and growing family of 2D materials, and it was named the new wonder material.[1, 2]

Many superlatives were used to describe the properties of graphene, a result of its ultimate flatness, a thickness of one atom. Soon, scientists envisioned significant improvements to the performance of transistors, touch screens, gas and light sensors, solar cells, batteries, and much more.[3, 4] The predictions of the science community about graphene were taken seriously by funding organizations and companies, resulting in an enormous increase in research and patenting activities. Mass production of graphene is now established - though maybe not yet in its highest quality form - and the first graphene application are slowly entering the markets.[5] Nonetheless, it will still take several years and probably even longer to see the true impact of graphene for industrial applications.

In the mean time, and perhaps more importantly, graphene continues to provide physicists with new fundamental phenomena to explore. In this thesis I present experiments that, hopefully, contribute to these explorations into the properties that make graphene such a promising material.

Graphene electrons To understand more about why graphene has such special properties compared to conventional materials and why it shows such interesting physics, one has to look at its structure. A substantial part of its properties relates to the way the electrons are ordered in the 2D crystal. Examples of such properties that can be directly linked to the electronic structure, include a high electrical conductivity and an equal absorption of all colors of light.

The special electronic behavior of graphene is determined by its *dispersion relation*. This relation describes the electron energy E and its dependence on the wave vector k, associated with the momentum of the electron. In graphene, the electron energy for the free electrons (the ones that can move around) is linearly dependent on k, while in most solid matter this dependence is approximately parabolic. Due to the specific linear dispersion, electrons travel at a constant, very high speed through the

material and are very insensitive to scattering, making graphene very suitable for uses in electronic circuits.

A description of all the electron orbitals in a crystal is given by its *band structure*, which is a diagram that gives the dispersions of all electrons. Fig. 1.1 shows two examples of such a band diagram, zoomed in on the free electrons, or transport electrons. These electrons have the highest energy, around an energy level called the Fermi energy E_F. The band structure of graphene looks like an hourglass: two cones that touch with their tips. In neutral graphene, E_F is exactly at the touching point, called the charge neutrality point or *Dirac point*, as is depicted in Figure 1.1(b).
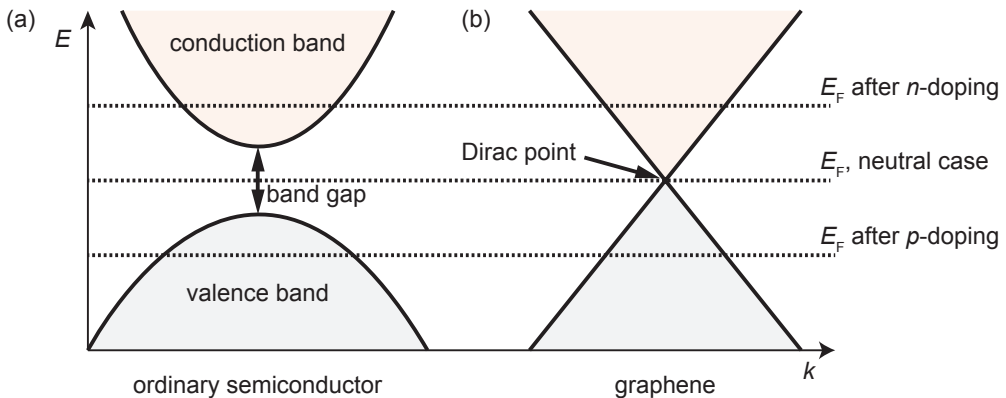

Figure 1.1: Band structure around the Fermi energy E_F, the energy level of the transport electrons. (a) In ordinary semiconductors, E_F lies in between the valence and the conduction band, but can be shifted by adding dopants, which are elements that donate or accept electrons to the bulk material. For acceptors (*p*-dopants) the transport becomes hole-like. For donors (*n*-dopants), the transport becomes electron-like. (b) In graphene, E_F can be significantly shifted using an electrostatic potential. Thus, graphene has a strong gate effect, meaning that its resistance and even the carrier type (electron or hole) can be changed using an external electric field.

The touching of the electronic bands makes graphene a zero band gap semiconductor. To understand this, compare the two diagrams in Fig. 1.1. In ordinary semiconductors, E_F lies in the band gap, which is the energy range where there are no orbitals available for electron transport. E_F can be shifted by adding charge acceptors or donors. This process, called *doping*, controls the number of charge carriers and even their type. If E_F lies in the conduction band, negatively charged electrons are responsible for charge transport. If E_F lies in the valence band, charge is carried by holes, which are empty electron orbitals that behave like particles with positive charge. In graphene, it is possible to shift E_F and thus switch between electron and hole transport by applying an external potential (electrostatic gating). Therefore, graphene has the very special property that the number and type of charge carriers

can be tuned without the use of dopants.

The electronic properties of graphene also give rise to a variety of exotic phenomena that are associated with the quantum mechanical nature of the electron wave function. Such phenomena were previously only available in 2D electron gases, which exist at interfaces between different materials. A famous example is the quantum Hall effect, which arises in regular 2D electron gases at low temperature when the electron paths are bent into circular orbits by the influence of strong magnetic fields. As a result, the electrons only conduct along the edges and have energies that increase only in discrete or "quantized" steps. Because the electronic structure of graphene is so robust, it shows (a special version of) the quantum Hall effect even at room temperature.[6, 7]

The room temperature quantum Hall effect in graphene is just one example of the new physics that can be studied in graphene, a result of the truly uniques behavior of its electrons. Thus, graphene is a complex, but very rich and fascinating subject for the experimental physicist.

Epitaxial graphene To make graphene in the lab, researchers mostly use the sticky tape method mentioned in the beginning of this chapter. These exfoliated graphene flakes are popular because of their high structural quality, but are typically very small and the production is time-consuming. For large scale applications it would be desirable to produce graphene with increased area, with lower costs per unit area and a higher production rate. Fortunately, there is a range of production methods to choose from. One has to take into account that the specifics of each production method have a direct effect on the resulting graphene properties. In practice, each application will have its own trade off between material properties, cost and production time.

From an experimental point of view it can also make sense to use large area graphene. Upscaled and well-controlled growth generates the possibility to fabricate bigger and more complex circuits, but also to investigate their reproducibility.

One method to create large area graphene is by the decomposition of silicon carbide (SiC) at high temperatures, which allows for controlled, layer-by-layer growth of graphene directly on the SiC substrate. The result is called epitaxial graphene, because the graphene is correlated with the underlaying SiC crystal, resulting in a good structural quality. Another advantage of this production method is the fact that the SiC substrate is an insulator, so it does not short circuit the graphene, which is an important condition for uses in electronics. Epitaxial graphene on SiC has a very good quality, but also has high production costs due to the relatively expensive SiC. Nonetheless, epitaxial graphene on SiC is very promising for future high-end electronic devices, such as sensors and high frequency transistors, where performance is more important than low cost.

1.1   Scope of this thesis

In this thesis, I investigate spintronic and thermoelectric effects in graphene, which are phenomena that involve electron transport. In conventional electronics, electrons can be moved from A to B by using electrostatic potentials (the voltage of a battery for instance). Electrons follow these electric fields, because they have a charge of $-e$ each. The strength of the field of electronics lies in the fact that these manipulations can be done relatively easy in wires and circuits. But there are ways to influence the path of an electron that travels through a solid piece of material, by making use of other properties than charge. One of these properties is spin, the fact that each electron has an intrinsic magnetic moment with an absolute value of approximately μ_B, called the Bohr magneton. Magnets and magnetic fields can be used to transport and manipulate electron spins. The creation and manipulation of spin currents is studied in the field of spintronics. In graphene, spin currents can exist for a relatively long time, making it an interesting spintronic material. In this thesis, I present studies on the specific spin transport properties in large area graphene that is grown on a silicon carbide substrate.

Besides charge and spin, it is also possible to use the electron energy or, equivalently, its heat. Electrons flow from hot places to cold places to average out their temperature and reach thermal equilibrium. However, the presence of temperature gradients affect the flow of charges and, vice versa, electric fields effect the flow of heat. This is called thermoelectrics. A well-known example of a thermoelectric phenomena is called the Peltier effect, which is the heating or cooling of an interface between two different materials by sending a current through it. In this thesis, I will present experiments showing that if one of these materials is graphene, the heating or cooling can be controlled by a gate voltage.

These studies are interesting, because they are ways to experimentally gain insight about fundamental topics in physics like magnetism, thermodynamics and mesoscopic transport, in a relatively new system with low dimensionality. For future applications, one wants to go a step further: not only understand, but actively control and manipulate charge, spin and heat flows in materials on the nanometer scale. Ideally, this would result in smaller, faster and more energy efficient electronic devices and, even better, completely new devices functionalities. These can include new (spin) logic circuits that can be integrated with magnetic data storage (currently used in hard disks) and control over heating effects in nanoscaled devices.

1.2   Outline

This thesis is divided into two parts. Part I (Chapters 2-4) discusses some concepts that are useful in the understanding of Part II (Chapters 5-9), the experimental section.

Part I: Theoretical background   In **Chapter 2**, I explain the basics of spin trans-
port and the tools that are commonly used to study spin transport properties in
graphene. These include the nonlocal spin valve and Hanle experiments, that use an
in-plane and out-of-plane magnetic field respectively, to determine the properties of
spin diffusion and spin relaxation. I end the chapter with a short overview of the
field of graphene spintronics. In **Chapter 3**, I start with a general description of the
Seebeck and the Peltier effect, two fundamental aspects of thermoelectrics, that de-
scribe the interaction between charge and heat transport. After a short introduction
into graphene's heat transport properties, I continue with a description of graphene
thermoelectrics.

Because a large part of the experimental section involves large area graphene on
silicon carbide (SiC), I dedicate **Chapter 4** to an overview of the current state-of-
the-art in graphene growth, a description of its characteristics and its potential for
applications.

Part II: Experiments   The second part of this thesis consists of 5 chapters, each
dedicated to an experimental project that has been published, or soon will be, in
peer-reviewed scientific journals.

The first four experimental works I carried out within the scope of the EU Seventh
Framework program named ConceptGraphene, which had the aim of investigating
the potential of large-area graphene on SiC for the use in non-conventional electronic
devices and circuits. My contribution was to investigate and report its possible use in
spintronics. I show the first realization of spin valve and Hanle precession measure-
ments in graphene on SiC in **chapter 5**. I show, that these properties are unexpectedly
different from those in "regular", exfoliated graphene, which shows up in a remark-
ably narrowing of the Hanle curve. In **chapter 6**, I show that these differences are
related to the buffer layer that is typically found in graphene on SiC samples, and
I present a model of localized states in the buffer layer, that should be considered
when analyzing Hanle experiments. In **Chapter 7**, I demonstrate that the effect of
the buffer layer can even result in a drastic change in the shape of the Hanle curve in
such a way, that conventional analysis of the Hanle experiments no longer applies.
Then, in **chapter 8**, I present an extension on the localized states model, that assumes
that the localized states have a continuous distribution of different coupling rates,
and I use this model to gain better insight in what processes are involved in the cou-
pling of the localized states and the spin channel. In **Chapter 9**, I investigate epitaxial
graphene on the carbon terminated face of the SiC crystal, a system without a buffer
layer, where I show that localized states can also have a similar, though weaker, effect
on the spin transport measurements.

In **Chapter 10**, I present measurements of the cooling and heating of a graphene-
gold interface by using the Peltier effect. In contrast to the other experimental chap-
ters, this work was done using exfoliated graphene, because an important aspect of
these experiments is active gate control over the charge carriers. I show that we were

able to reverse the cooling and heating effect by tuning between electron and hole transport.

To conclude my introduction, I wish you great pleasure and new insights when reading this thesis, whether you plan to briefly scan or intensively study it.

References

[1] A. K. Geim and K. S. Novoselov. 'The rise of graphene'. *Nature Materials* **6**, 183 (2007).

[2] A. K. Geim and P. Kim. 'Carbon Wonderland'. *Scientific American* **298**, 90 (2008).

[3] K. S. Novoselov, V. I. Fal'ko, L. Colombo, *et al.* 'A roadmap for graphene'. *Nature* **490**, 192 (2012).

[4] A. C. Ferrari, F. Bonaccorso, V. Falko, *et al.* 'Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems'. *Nanoscale* (2014).

[5] M. Segal. 'Selling graphene by the ton'. *Nat Nano* **4**, 612 (2009).

[6] K. S. Novoselov, A. K. Geim, S. V. Morozov, *et al.* 'Two-dimensional gas of massless Dirac fermions in graphene'. *Nature* **438**, 197 (2005).

[7] Y. Zhang, Y.-W. Tan, H. L. Stormer, *et al.* 'Experimental observation of the quantum Hall effect and Berry's phase in graphene'. *Nature* **438**, 201 (2005).

Part I

Background