

MASTER THESIS

# Towards Ferromagnetism in Hydrogenated Epitaxial Graphene on Silicon Carbide

Author: Maurits J. de Jong s1795562

Daily Supervisor: ir. J. J. van den Berg Group Leader: prof. dr. ir B. J. van Wees

Co Referent: prof. dr. ir. R. A. Hoekstra

Physics of Nanodevices Zernike Institute for Advanced Materials University of Groningen January 24, 2015

### Abstract

Since the discovery in 2004, the 2-dimensional material graphene is widely investigated. Graphene combines many extraordinary properties in different areas like mechanical, electronic and magnetoelectric properties, making it an interesting material to study. Giesbers *et al*, Reference [1], have claimed that it is possible to induce ferromagnetism in epitaxial graphene on sillicon carbide by hydrogenation. It would be interesting to study the effect of ferromagnetism on transport properties of graphene in a device geometry.

In this work, we investigate three experimental methods for the hydrogenation of epitaxial graphene on sillicon carbide. Method I consist of exposing the graphene to hydrogen plasma. Method II consists of exposing the graphene to an atomic hydrogen beam at room temperature, which has been made using radio frequency radiation. The last method, Method III, consist of exposing graphene to an atomic hydrogen beam, which has been made by thermal cracking of  $H_2$ -molecules.

The effectiviness of the experimental hydrogenation methods are investigated using magnetic and atomic scanning probe microscopy, raman spectroscopy and electronic and magnetoelectric transport measurements.

Method I and Method II did not provide clear or strong evidence of successful hydrogenation in the scanning probe and transport measurements. Graphene that was exposed to an atomic hydrogen beam of Method III did initially, right after the hydrogenation step, show strong indications of carbon-hydrogen bonds. Over time, some of the carbon-hydrogen bonds seemed to dissociate from graphene.

Since hydrogenation Method III did show carbon-hydrogen bonds, this method seems to be the most promising method to bind hydrogen atoms to the graphene. However, in contradiction with Reference [1], no ferromagnetic domains were encountered after exposing the graphene sample to the atomic hydrogen beam. Furthermore, the amount of carbon-hydrogen bonds seemed to decrease over time. More research is needed to identify all parameters of the hydrogenation step the carbon-hydrogen bonds on permanent. This includes the exact temperature and pressure of the atomic hydrogen beam and the duration of the exposure. The creation of ferromagnetic domains by an interaction of the hydrogen atoms bonded to the graphene can than be investigated in more detail, perhaps in combination of lithography processes.

## Contents

1	Intr	Introduction					
<b>2</b>	Theory						
	2.1	Graphene	4				
		2.1.1 Epitaxial Graphene on Silicon Carbide	$\overline{7}$				
	2.2	Magnetism in Graphene	9				
		2.2.1 Magnetic Properties in Transport	10				
3	$\mathbf{Exp}$	perimental	<b>14</b>				
	3.1	Device fabrication	14				
		3.1.1 Electron beam evaporation	14				
		3.1.2 Reactive ion etching	15				
		3.1.3 Photolithography	15				
	3.2	Hydrogenation methods	17				
		3.2.1 Hydrogenation method I: hydrogen plasma	17				
		3.2.2 Hydrogenation method II: radio frequency atomic hydrogen	17				
		3.2.3 Hydrogenation method III: radio inequency atomic hydrogen	18				
	22	Seanning probe migroscopy	10				
	ა.ა	2.2.1 Atomic force microscopy	19				
		3.3.1 Atomic force microscopy	19				
		3.3.2 Magnetic force microscopy	19				
	3.4	Raman spectroscopy	21				
	3.5	Transport measurements	23				
		3.5.1 Lock-in amplifier	23				
		3.5.2 Electronic measurements	23				
		3.5.3 Magneto-electric measurements	24				
4	ъ	14	05				
4	Res	ults	25				
	4.1	Hydrogenation Method I: hydrogen plasma	25				
		4.1.1 Scanning probe microscopy	25				
		4.1.2 Transport measurements	27				
		4.1.3 Conclusion	27				
	4.2	Hydrogenation Method II: radio frequency atomic hydrogen beam	29				
		4.2.1 In situ resistance measurements	29				
		4.2.2 Scanning probe measurements	30				
		4.2.3 Transport measurements	31				
		4.2.4 Conclusion	32				
	4.3	Hydrogenation Method III: atomic hydrogen beam by thermal cracking	33				
		4.3.1 Scanning probe measurements	33				
		4.3.2 Raman spectroscopy	35				
		4.3.2 Conclusion	36				
			00				
<b>5</b>	Con	nclusion	37				
	5.1	Conclusion	37				
		5.1.1 Hydrogenation by Hydrogen Plasma	37				
		5.1.2 Hydrogenation by Atomic Room Temperature Hydrogen Gas	37				
		5.1.3 Hydrogenation by Atomic Hydrogen Gas by a Thermal Cracker	37				
	5.2	Overall Conclusion and Prospects	38				
6	Acknowledgments 39						
Re	References						

### 1 Introduction

Peierl and Landau argued, in 1935 and 1937 respectively, that it is not possible that a pure 2D-material can exist or be manufactured. A 2D material will be thermally instable and will break or transform into a non-2D material, by wrinkling or rolling up. Nevertheless, Geim and Novolesov were able to manufacture graphene in 2004[2], the one atom thick carbon based material, using the sticky tape mehod. Graphene was isolated by pulling off layers of carbon atoms from graphite with Scotch tape, clearing repeatedly, until one layer of carbon atoms remained. After the microcleavage, the graphene was transferred to SiO<sub>2</sub>. Since then the research in 2D-materials and especially the research on graphene has expanded rapidly, which resulted in the Nobel-prize for physics in 2012, awarded to Geim and Novolesov.

Every year, new and extraordinary properties are discovered for graphene or graphene based materials and it is considered now as one of the most promising materials in the material sciences and condensed matter physics[3]. Graphene is the strongest known material, with a Young's modulus in the order of 1 TPa, 100 times stronger than steel[4]. This phenomena is illustrated in the Nobel announcement, stating that a sheet graphene of 1 m<sup>2</sup> will support the weight of a cat of 4 kg, but will weigh less than 0.77 mg, or 0.001 % of 1 m<sup>2</sup> of paper[5]. The applications for a material with this tensile strength are enormous, for instance extreme weight reduction for constructions. Furthermore, graphene combines this strength with a high stiffness and elasticity. Graphene has more notable properties, for instance that it has a high thermal conductivity[6] and the fact that a graphene sheet is impermeable for gasses[7].

Graphene also has exceptional electronic and spintronic properties. It has a high carrier mobility, *e.g.* it can carry current densities a million times higher than copper. Furthermore, graphene has a small spin-orbit interaction at room temperature, a long spin relaxation length, in the order of a few micron, and a long spin relaxation time, in the order of a few hundred picoseconds. This makes it possible to measure spin current at room temperature[8]. Moreover, the properties of graphene can simply be adjusted or tuned by adding some defects in pristine graphene[3].

Graphene combines thus many superlative properties in one material, so that graphene is potentially a useful material for research in spintronic devices. Magnetic moments influence the spin relaxation length, the spin relaxation time and thus the spin current. Therefore magnetic properties of graphene and the effect on magnetic moments caused by defects or adatoms like fluorine, chlorine and hydrogen, are given a lot of attention[9]. Adatoms create magnetic moments that lead to paramagnetism, but it is very difficult to make graphene ferromagnetic through adatoms. However, recently, it is reported that hydrogenated epitaxial graphene on silicon carbide showed ferromagnetic properties[1] [10], which makes it an interesting material to study.

The thesis will investigate different hydrogenation methods and the possibility of ferromagnetic properties of carbon-hydrogen bonds on hydrogenated epitaxial graphene on silicon carbide. This is done by exposing different epitaxial graphene on  $SiO_2$  samples to three different hydrogenation methods: exposure to hydrogen plasma made in a reactive ion etching system, exposure to an atomic hydrogen beam at room temperature and exposure to an atomic hydrogen beam, made by thermal cracking. Afterwards, the graphene samples are investigated after exposure, using scanning probe microscopy, transport measurements and Raman spectroscopy, to check if the method was successful. The thesis treats in the second chapter first some theory on graphene, epitaxial graphene and magnetic properties of graphene. The third chapter explains the experimental setups and methods and the fourth chapter shows the results of the experiments.

### 2 Theory

This chapter will cover the basic theoretical concepts of graphene. We discuss the structure of graphene and of a silicon carbide substrate. We also treat magnetic properties and the influence of magnetic properties on (spin) transport phenomena in graphene.

### 2.1 Graphene

Graphene is a 2-dimensional material made of carbon atoms, that are ordered in a hexagonal honeycomb like crystal structure. This creates a sheet of one atom thick, which consists of repeating benzene rings. Since graphene is purely made of carbon atoms, it can be used as a start material to build other carbon-based materials like Buckeyballs (0D-material) and nanotubes (1D-material), which is illustrated in Figure 1. Multiple graphene layers stacked on top of each other and held together with van der Waals' forces create graphite, the same material from which the first freestanding graphene layer is isolated using the sticky tape method[2]. The sticky tape method consists of lifting a graphene layer from graphite with adhesive tape, after which it is transferred to a silicon carbide wafer.



Figure 1: Graphene is a 2D building material for carbon materials of all other dimensions. It can be wrapped up into 0D buckyballs (left), rolled into 1D carbon nanotubes (middle) or stacked into 3D graphite (right). Image taken from [11]

Each unit cell of the lattice of graphene consists of two carbon atoms, which is visualized in Figure 2. The two lattice vectors of this hexagonal structure can be written as:

$$\vec{a}_1 = a_0 \sqrt{3} (\frac{1}{2}, \frac{\sqrt{3}}{2}) 
\vec{a}_2 = a_0 \sqrt{3} (-\frac{1}{2}, \frac{\sqrt{3}}{2})$$
(1)

Here,  $a_0$  is the nearest neighbour distance of carbon atoms,  $a_0 = 1.42$  Å [13]. P. R. Wallace was



Figure 2: Schematic image of the crystal lattice of graphene. Carbon atoms are located at each crossings and the lines indicate the chemical bonds, which are derived from  $sp^2$ -orbitals. Also shown are the primitive lattice vectors  $\vec{a}_{1,2}$  and the unit-cell (shaded). There are two carbon atoms per unit cell, numbered 1 and 2. Image taken from [12].

the first to calculate the bandstructure of a single layer of graphite in 1947[14]. The calculation demonstrated that graphene is a zero-gap semiconductor.

The carbon atoms in graphene have each four valence electrons and four corresponding valence orbitals, the 2s,  $2p_x$ ,  $2p_y$  and  $2p_z$  orbitals. From this four orbitals, three are used for the  $sp^2$  carbon-carbon bonds and are oriented in the xy-plane, where the nearest neighbor carbon atoms are separated by an angle of approximately 120°, creating the previously mentioned honeycomb structure. The last electron, with the  $p_z$ -orbital, is free and delocalized over the entire graphene crystal. This orbital contributes to the  $\pi$ -band. Since there are two carbon atoms per unit cell, there are also two  $\pi$  orbitals per unit cell: the  $\pi$  and  $\pi^*$ -orbital which are pointed in the z- or -z-direction of the unit cell.

The  $\pi$ -band electronic dispersion of the 2D hexagonal Brillouin zone behaves linearly around the K and K' points. This linearity creates the cones at the six corners of graphene in the Brillouin zone, which can be seen in Figure 3b. These cones are called the Dirac points of graphene. The cones are described by Equation 2.

$$E = \hbar v_F \sqrt{k_x^2 + k_y^2} \tag{2}$$

Here is  $v_F$  the Fermi-velocity of the charge carriers near the Dirac points and is in the order of  $v_F \approx 10^6 \text{m/s}$ . Linear dispersion at the Dirac points results in particles having zero effective mass, *i.e.* the charge carriers in graphene behave as massless particles or Dirac fermions.

The fact that the charge carriers in graphene can be treated as effectively massless Fermions and that charge carriers can move freely in two dimensions, results into that the electronic properties of graphene are almost the same as for a 2D gas of charged particles[16].

The linearity of the bandstructure in Figure 3b and the fact that it is a zero-gap semiconductor, makes it possible to change the carrier density or type of charge carrier, *i.e.* electrons or holes, by raising or lowering the Fermi energy. In a device geometry, this is achieved by applying a back gate voltage.

Furthermore, the charge carriers can move around freely in pristine graphene. Due to the fact that they accumulate an extra phase, the Berry phase, after moving around in a closed loop, weak



Figure 3: (a) Energy bands near the Fermi level in graphene. The conduction and valence bands cross at points K and K'. (b) Conic energy bands in the vicinity of the K and K' points. (c) Density of states near the Fermi level with Fermi energy  $E_F$ . Image taken from [15]

antilocalization is expected in graphene[17]. After the charge carrier has finished a closed loop in the opposite direction, it meets counter-propagating charge carriers in anti phase, caused by the Berry phase. This leads to destructive interference effects of the charge carriers resulting in a lowering of the resistivity. The contribution of spin-orbit coupling to weak antilocalization is neglectable small[17].

If a source of elastic scattering is introduced, it is possible that graphene exhibits weak localization scattering. This elastic scattering can change the momentum of the charge carriers, which will change the phase of the wave function of the corresponding charge carrier.

Overall, the electronic transport can simple be described with the Drude model. The Drude model uses the kinetic theory of gases to the electron motion in solids. The theory assumes that the electrons behave as they were independent, free particles that respond to external forces, like external magnetic (**B**) or electric (**E**) fields. Once equilibrium is reached, electrons move with an average velocity (v), which can be found using the equation of Newton:

$$\frac{d\mathbf{v}}{dt} = -\frac{e}{m^*} (\mathbf{E} + \mathbf{v} \times \mathbf{B}) - \frac{\mathbf{v}}{\tau} = 0$$
(3)

Where e is the electron charge,  $m^*$  the effective mass of the electrons,  $\tau = \frac{v}{\lambda}$  is the relaxation time and  $\lambda$  the mean free path of the electrons. The electron current density is related to the drift velocity of the electrons v by:

$$J = env \tag{4}$$

Where n is the electron carrier density. In two dimensions, Formula 3 can be written as:

$$\mathbf{E} = \rho \mathbf{J} = \begin{pmatrix} \rho_{xx} & \rho_{xy} \\ \rho_{yx} & \rho_{yy} \end{pmatrix} \mathbf{J} = \sigma_0^{-1} \begin{pmatrix} 1 & -\omega_c \tau \\ -\omega_c \tau & 1 \end{pmatrix} \mathbf{J}$$
(5)

Where  $\sigma_0 = ne^2 \frac{\tau}{m^*}$  is the Drude conductivity and  $\omega_c = \frac{eB}{m^*}$  the cyclotron frequency. With no magnetic field, Formula 5 will become Ohm's law,  $\mathbf{E} = \sigma_0^{-1} \mathbf{J}[18]$ .

### 2.1.1 Epitaxial Graphene on Silicon Carbide

Nowadays there are different ways to manufacture graphene. A widely used method for graphene fabrication is the previously described sticky tape method to isolate exfoliated graphene from graphite[2]. Another method to manufacture graphene is the epitaxial growth on silicon carbide (SiC), by a sublimation process.

The silicon carbide used to grow graphene has a hexagonal crystal structures. The types 4H SiC and 6H SiC are mostly used to grow epitaxial graphene. If the hexagonal crystal structure of SiC repeats itself after four layers, it is called 4H SiC and if the hexagonal crystal structure of SiC repeat itself after 6 layers it is called 6H SiC. This is visualized in Figure 4.



Figure 4: Stacking sequence of the crystal structure of silicon carbide. Silicon is here white and carbon is here black. a) 4H SiC. The layers of silicon carbide with a stacking sequence of ABCB. b) 6H SiC. The layers of silicon carbide with a stacking sequence of ABCACB. Image taken from [19]

To grow epitaxial graphene, the silicon carbide is heated up to a high temperature (1100°C - 2000°C) [20, 21, 22, 23, 24, 25]. The silicon atoms begin to sublimate from the top layer, leaving behind the carbon atoms. If all parameters as temperature, pressure and heating time are optimal, the remaining carbon atoms will form two new layers, arranged in the hexagonal configuration of graphene. The lowest layer is the interface or buffer layer, which does not show the characteristic  $\pi$ -bands of pristine graphene. This is caused by the covalent bonds between the buffer layer and the remaining silicon carbide[26]. The top-layer is monolayer graphene, bound to the buffer layer by 'van der Waals'-forces, which is visualized in Figure 5.

The graphene layer on top of the silicon carbide has the  $6\sqrt{3} \times 6\sqrt{3}R30$  configuration. *I.e.* the lattice of the crystal structure of graphene combined with the bufferlayer and silicon carbide substrate is  $6\sqrt{3}$  times larger than the lattice of silicon carbide and is oriented  $30^{\circ}$  off with respect to the crystal structure of silicon carbide. Because of the lattice mismatch between the buffer layer and the silicon carbide, substrate not all atoms of the buffer layer can make a covalent bond with the silicon carbide , resulting in a dangling bond through the unpaired electrons.

The top layer of the silicon carbide will not be completely flat, because there exist a miscut angle with respect to the crystal lattice. The surface of the silicon carbide is in this way stairlike, where each step is formed by a terrace. The miscut angle influences the width of the different terraces, but the terraces are mostly in the order of a few microns. During the sublimation proces, the silicon atoms at the edges between two terraces will sublimate more easily than the silicon atoms in middle of the terraces. Therefore, a second layer of graphene will be present at the terrace edges, making a substrate uniformily covered with a monolayer very difficult. This is schematically



Figure 5: The graphene (grey top layer) is bound to a buffer layer by van der Waals' forces. The bufferlayer (middle grey layer) itself is bound to the silicon carbide substrate (black (silicon) and grey (carbon)) by covalent bonds.

visualized in Figure 6.



Figure 6: The stairlike toplayer of graphene. Different terraces make up the surface, with some bilayer parts at the terrace edges. Despite the different thickness around the terrace edges, the graphene is continuous over the whole region.

### 2.2 Magnetism in Graphene

Pristine graphene itself is mainly diamagnetic, which is similar to graphite. Graphene only shows at low temperatures (< 50 K) a small background of paramagnetic behavior. Ferromagnetism is not detected in pristine graphene, even at a temperature of 2 K[27]. Point defects caused by adatoms or vacancies, can carry a magnetic moment and thereby increasing the magnetization. Vacancies can be made in graphene using irradiation techniques[28]. The Kondo effect, the scattering of charge carriers on magnetic impurities, and the giant negative magnetoresistance, a decrease in resistance for increasing magnetic field, are reported in graphene devices with these kind of defects[29]. The vacancies in the graphene create paramagnetic moments, which will cause more intervalley scattering, resulting in more insulating behavior and thus a higher resistivity.

Adding donor atoms to the graphene, will change the orbital that contributes to the  $\pi$ -band in a sp<sup>3</sup> bond. These adatoms should have enough energy to overcome the energy barrier of the  $sp^2$ bond between the carbon atoms, ~ 2.7 eV[30], to form the new  $sp^3$  bond. By forming the new  $sp^3$ bond, the band gap is changed to 3.5 eV[31]. Furthermore, adding an adatom changes locally the magnetic moment. Through the adatom, short-range potentials will cause intervalley scattering. The intervalley scattering allows the counter propagating charge carriers to occupy a different valley in the electronic band structure, which results in restoring the weak localization. The two charge carriers will be in phase with their wave function, creating constructive interference. A direct consequence is that the graphene will become more insulating and the resistance will increase [17, 32, 18]. The most used adatoms which have a significant effect on the magnetization and weak localization are fluor and hydrogen atoms[33] [34]. These adatoms give mostly a local paramagnetic magnetization to the material.

Hydrogenation, the proces to add hydrogen atoms, of graphene is now a major area in the graphene research[10, 35]. During the hydrogenation step, the graphene is exposed to a hydrogen gas or plasma and carbon-hydrogen bonds are created. The hydrogen atoms that have enough kinetic energy can convert the  $p_z$ -orbital of the delocalized electrons that contributes to the  $\pi$ -band in a  $sp^3$  bond between a carbon and hydrogen atom. The hydrogen atoms are placed in the direction of the  $p_z$ -orbital. Hydrogenated exfoliated graphene is paramagnetic and will change from a zero-gap semiconductor to more insulating, due to the decrease of delocalized electrons. Furthermore, the hydrogenation proces is often completely reversible, by annealing the hydrogenated sampleand so dissociating the hydrogen atoms from the graphene[36].

Recently, Giesbers *et al* showed that binding hydrogen atoms to epitaxial graphene on silicon carbide exposed to atomic hydrogen gas for 3 minutes, results in ferromagnetic domains at a temperature of 300 K. Figure 7a shows a ferromagnetic hysteresis loop for different magnetizations of the sample, which was measured using a superconducting quantum inference device (SQUID). To check if the ferromagnetic properties are caused by hydrogenated graphene with a bufferlayer on silicon carbide, different control samples were made for comparison. The first one, is silicon carbide with graphene (SiC+G), where the sample was not exposed to the atomic hydrogen beam. To check the effect of the bufferlayer, quasi-freestanding monolayer graphene, untreated (QFMG) and hydrogenated (hQFMG), were investigated. Quasi-freestanding monolayer graphene is manufactured using hydrogen intercalation, the procedure to add hydrogen atoms to the substrate underneath the bufferlayer. This ensures that the bufferlayer has no covalent bonds with the silicon carbide substrate and behaves like normal graphene[35]. Furthermore bilayer epitaxial graphene on silicon carbide is investigated, untreated (BL) and hydrogenated (hBL). The last control sample is a pure silicon carbide substrate (SiC). The geometry of the control samples are further visualized in Figure 7b. The fact that the hydrogenated epitaxial graphene is the only sample that exhibits ferromagnetic properties is probably caused by the bufferlayer. The hydrogen-atoms were bond to the graphene on top of the bufferlayer, the bufferlayer itself appeared to exhibit paramagnetic behavior.

Besides measurements with a SQUID, Giesbers *et al* investigated the ferromagnetic properties using a magnetic force microscope, which measures the magnetic phase difference. (See Section 3.3.2 for information about magnetic force microscopy.) Figure 8 shows the phase difference of the magnetic domains. The phase difference is caused by different magnetizations on monolayer



Figure 7: a) Magnetization for different control samples as function of an external magnetic field. Hydrogenated epitaxial graphene with a bufferlayer on silicon carbide (black) is the only sample that shows the for ferromagnetism characteristic hysteresis loop. b) Schematic representations of various control samples. QFMG: quasi-freestanding monolayer graphene, where the graphene layer is made quasi-freestanding by intercalation of hydrogen atoms between the SiC substrate and the bufferlayer. hQFMG: hydrogenated quasi-freestanding monolayer graphene. BL: SiC substrate with only the bufferlayer. hBL: hydrogenated bufferlayer on SiC substrate. Image taken from [1]

graphene (1L) and bilayer graphene (2L). Hydrogen will bond more easily to monolayer graphene than to bilayer graphene. The different coverage and thus  $sp^3$  bonds distribution results in different magnetic moments between the terraces and around the terrace edges. Another explanation is the contribution of a different electronic structure in bilayer graphene or due to the increased distance between the hydrogenated bilayer graphene and the bufferlayer the interaction between hydrogen sites and the bufferlayer will be different. The switching of the out-of-plane remanent magnetization is clearly visible in the cross sections in Figure 8c. Specifically, with a positive magnetization, the MFM signal is positive and the signal from the single layer graphene is slightly larger than the signal from the bilayer graphene. With a negative magnetization, the MFM signal has reversed the sign and signal from the single layer graphene is again higher, in absolute terms. These changes show that the color inversion between Figure 8a and Figure 8b is due to a complete flip of the magnetization direction, while the signal from the single layer graphene is always higher than that from the bilayer graphene. That the flip of magnetization is not symmetric around zero for Figure 8c indicates that there is also a constant background phase shift present.

It is proposed that the ferromagnetic domains can be interpreted in terms of an exchange coupled interaction between localized electron states of the buffer-layer and either spin-polarized localized states or the mid-gap states of the hydrogenated graphene layer[37]. A second possibility is that the hydrogenated graphene on top of the bufferlayer is intrinsically ferromagnetic, but with a much lower Curie temperature, since it is 2D. If the paramagnetic bufferlayer will exchange couple to this ferromagnetic graphene layer, it will become quasi-3D and the exchange coupling will increase the Curie temperature [1]. The exact mechanisms behind the ferromagnetic behavior of hydrogenated epitaxial graphene is still under active investigation, which is also one of the motiviations for this study.

#### 2.2.1 Magnetic Properties in Transport

Hydrogen atoms that are added to graphene generate magnetic moments. For most kinds of graphene (exfoliated, epitaxial et cetera) the effect of adding a hydrogen atom results in paramagnetic properties. Epitaxial graphene on silicon carbide exhibits however ferromagnetic properties. This unique property can be investigated using spin current measurements, for instance a nonlocal



Figure 8: a)Magnetic force micrograph of hydrogenated epitaxial graphene after applying a positive magnetic field to the sample showing high and low remanent magnetization for single and bilayer. b) Inversion of the remanent magnetization after applying a negative magnetic field to the sample. c) Cross section of the positive (a) and negative (b) magnetization. Image taken from [1]

spin valve. The geometry of such a device is pictured in Figure 9.



Figure 9: A nonlocal spin valve.

In the nonlocal four-probe spin value of Figure 9, a current I is injected from the ferromagnetic electrode 2 through the tunnel barrier into the graphene. The current is extracted at electrode 1. At the same time the voltage difference between electrode 3 and 4 is measured, which is used to calculate the nonlocal resistance using Equation 6.

$$R_{nonlocal} = \frac{V_3 - V_4}{I} \tag{6}$$

A nonlocal spin valve needs at least 2 ferromagnetic electrodes (for injection and detection), but more is also possible as illustrated in Figure 9. If the ferromagnetic contacts are placed directly on the graphene, the current will flow back into the electrode instead of flowing through the graphene to the next electrode. This backscattering is caused by the conductivity mismatch[38]. Caused, since graphene has a much higher resistance ( $\approx$  a few  $\Omega$ ) than the cobalt ( $\approx$  a few  $\Omega$ ) contacts. The current paths will be via the cobalt instead of the intended route through the graphene. A thin insulating oxide layer acting as a tunnel barriere will prevent the backflow of current to the cobalt injector contact. A disadvantage of a tunnel barriere is that a higher current has to be applied to inject the same amount of charge carriers due to transport losses by the tunnel barriere.

A spin current flowing through a diffusive conductor can be treated as two parallel independent spin channels, one for the spin up electrons and one for the spin down electrons[39]. This is the case when the spin orientation is unchanged under most scattering events to preserve the independence of the channels. The spin current density of the corresponding spin channels is proportional to the gradient of the electrochemical potential of a spin species. The dependence for spin up electrons is given by Equation 7.

$$j_{\uparrow} = \frac{\sigma_{\uparrow} \partial \mu_{\uparrow}}{e \partial x} \tag{7}$$

Here is  $\sigma_{\uparrow}$  the conductivity and  $\mu_{\uparrow}$  the chemical potential for the spin up channel.  $j_{\downarrow}$ , the spin current density of spin down, can be calculated in the same manner with  $\sigma_{\downarrow}$  and  $\mu_{\downarrow}$  respectively. The total current is given by  $I = j = j_{\uparrow} + j_{\downarrow}$  and the total spin current  $j_s$  is given by:  $j_s = j_{\uparrow} - j_{\downarrow}$ .

The conductivity of a ferromagnet,  $\sigma$ , can be separated in conductivity for the two corresponding spin species,  $\sigma = \sigma_{\uparrow} + \sigma_{\downarrow}$ . Using that the conductivity in a ferromagnetic has a surplus for one type of conductivity, *i.e.*  $\sigma_{\uparrow} \neq \sigma_{\downarrow}$ , a spin polarization p can be defined by means of the spin current or conductivity of the two spin species using Equation 7 in such way that Equation 8 is obtained.

$$p = \frac{j_{\uparrow} - j_{\downarrow}}{j_{\uparrow} + j_{\downarrow}} = \frac{j_{\uparrow} - j_{\downarrow}}{j}$$
$$= \frac{\sigma_{\uparrow} - \sigma_{\downarrow}}{\sigma_{\uparrow} + \sigma_{\downarrow}} = \frac{\sigma_{\uparrow} - \sigma_{\downarrow}}{\sigma}$$
(8)

Equation 8 can further be adjusted to:

$$j_{\uparrow} = (1+p)\frac{\sigma\partial\mu_{\uparrow}}{2e\partial x}$$

$$j_{\downarrow} = (1-p)\frac{\sigma\partial\mu_{\downarrow}}{2e\partial x}$$
(9)

Since a ferromagnet has  $j_{\uparrow} \neq j_{\downarrow}$ , it can be used as spin source for spin valves. Sending a current *I* through the ferromagnetic electrode, the injector, causes a spin accumulation in the non-magnetic material graphene. This accumulation decays exponentially with the distance from the injector:

$$\frac{\partial^2 \Delta \mu}{\partial x^2} = \frac{\Delta \mu}{\lambda_s^2} \tag{10}$$

Here is  $\lambda_s = \sqrt{D\tau_s}$  the spin relaxation length, D is the diffusion constant,  $\tau_s$  the spin relaxation time and  $\Delta \mu = \mu_{\uparrow} - \mu_{\downarrow}$ . If the detector is within the spin relaxation length  $\lambda_s$  from the spin injector, a spin valve resistance can be measured by applying a magnetic field and changing the ferromagnets from a parallel magnetization to an antiparallel magnetization. If the configuration is antiparallel, the spins of the spin current can easily enter the spin detector which leads to a lower spin valve resistance. When the configuration is parallel, the spin of the electrons has first to flip before they are able to enter the detector, which leads to a higher resistance. If the spins of the electrons of the spin current relax and reach uniform distribution before they can be detected by the ferromagnetic spin detector, only the average chemical potential equal to zero is measured. When the ferromagnets are switched from parallel to antiparallel orientation, the resistance of the spin valve will not change[40, 41].

It would be interesting to investigate a local ferromagnetic area in graphene, since it changes the  $\Delta \mu$  and influences the spin valve resistance. The magnetic moments generated by the hydrogen atoms cause a dip in the nonlocal spin signal as a function of the applied external magnetic field. This dip in the signal is caused by scattering or relaxation of pure spin currents by exchange coupling to the magnetic moments. For selectively hydrogenation of a specific graphene area, it



Figure 10: The effect of a local ferromagnetic area on spin current can be investigated by making a non-local spin valve locally ferromagnetic.

is necessary to develop a hydrogenation method which is compatible with lithography techniques. The ferromagnetic properties can than be investigated in a setup as Figure 10.

The fact the graphene can be made locally ferromagnetic can perhaps be used to make a contact in the graphene, see Figure 11. Since the contact has to be ferromagnetic, the area should also have a single magnetic domain. This ensures that the switching step will occur in a single step. Furthermure, since the ferromagnetic contact made in graphene and the graphene itself have both approximately the same conductivity, a tunnel barriere is not necessary, reducing the current losses.



Figure 11: Normally, in a non-local spin value with graphene, the electrodes have to be ferromagnets on top of a tunnelbarriere to work properly. If graphene can be made locally ferromagnetic, it will enable placing the electrodes in the graphene instead on top it.

### 3 Experimental

This chapter will treat the experimental part of the research. The methods for fabricating the devices, electron beam evaporation, reactive ion etching and photolithography, will be explained. The three hydrogenation methods that are investigated will be explained. Method I consists of exposure of the device to hydrogen plasma, method II consists of exposure of the device to an atomic hydrogen beam of room temperature which is made using a radiofrequency field and method III consists of exposure of the device to an atomic hydrogen beam of elevated temperature, which is made by thermal cracking. The last part of this chapter will treat the measurements that were done on the hydrogenated samples. This includes scanning probe measurements, Raman spectroscopy and various transport measurements.

### 3.1 Device fabrication

### 3.1.1 Electron beam evaporation

Electron beam evaporation is a technique to deposite thin films. First, the sample is placed upside-down in a vacuum chamber. Next, the desired deposition material, is placed in a water-cooled socket underneath the sample. Then this target is bombarded with an electron beam, which is deflected onto the target using a magnetic field. Since the material will heat up, particles will evaporate and condensate on the sample. With this technique it is possible to evaporate thin films with high precission and a rate of approximately 1 Å/s. The contacts of Figure 23a are made in the thin film coater using a shadowmask made of two strips of aluminum foil, which were positioned as a cross over the sample (horizontal and vertical). The structure of Figure 23b is first etched in the reactive ion etching-system with a Hall-bar shadowmask, after which a different shadowmask is used for coating the contacts on top of the graphene. The contacts were made by first applying a layer of 5 nm of titanium, after which the second layer of 35 nm of gold is applied.

The process is schematically visualized in Figure 12.



Figure 12: A schematic view of a electron beam evaporation system. The sample is placed in a vacuum chamber above the socket. An electron beam is directed to the material with the use of a magnetic field. The material will heat up and particles will evaporate from the surface. The evaporated particles condensate on the sample, creating a thin film. The socket is constantly cooled by water in order to keep the diffusion rate of the metal constant.

### 3.1.2 Reactive ion etching

Reactive ion etching is an etching method, that uses a low pressure plasma (e.g. oxygen), which is generated from a gas by applying an electromagnetic field. The ions in the plasma will react with the surface and etch away the toplayer. The sample is placed in a vacuum chamber on a wafer, which is electrically isolated from the rest of the chamber. The chamber is filled with gas, typically  $10^{-2}$  mbar, a strong electromagnetic field in the radio frequency (RF) domain is applied. Every time the field switches, the electrons are electrically accelerated up or down in the chamber, sometimes striking the walls or roof, causing the electrons of the particles to get absorbed. Since the wafer is more negatively charged by means of a DC-voltage, the positive ions are attracted to the wafer and thus to the sample. Through collision and kinetic energy transfer from the particles to the sample, some atoms of the surface have a big chance to be 'knocked out', or etched away (see Figure 13).



Figure 13: A schematic view of a reactive ion-etching system. The electromagnetic field accelerates the positive oxygen ions towards the negative electrode. If a higher DC voltage is applied to the electrodes, the electromagnetic field will be stronger and thus the kinetic energy of the ions will be higher. The shadow mask ensures that only a certain part of the sample is etched away.

For selectively etching a specific area on the sample, a shadow mask can be used to protect the surface underneath from any damage caused by the plasma. The flow of oxygen during etching is kept at 17 *sccm*, the sample was exposed to a plasma with a power of 40 Watt for 20 seconds.

The hydrogen-plasma used for hydrogenation method I is made in the RIE. A gas of 75% argon and 25% hydrogen is used. During exposure to the hydrogen plasma, the flow of argon/hydrogengas was kept at 200 *sccm*. The plasma was made using different voltages (0-9 V) between the electrodes and the power was kept at 0 Watt.

#### 3.1.3 Photolithography

Photolithography is a technique to create small patterns on a sample. These patterns can be used to create small structures of a certain material or to selectively etch away the substrate itself. The technique makes use of ultraviolet (UV) radiation and a light sensitive material, a photoresist. The photoresist is a sacrificial material, which is removed at the end of the lift off method with a solvent. To improve the lift off technique a double layer of photoresist can be used. In this way a small undercut is created, making it easier for the solvent to remove the remaining resist (Figure 14). To apply the photoresist, the sample is first heated at  $180^{\circ}$ C for 90 seconds. Next the PMMA 50k photoresist is coated on top of the sample using a spin-coater, using 4000 rpm for 60 seconds. Then the sample is heated for  $180^{\circ}$ C for 5 minutes, after which the second photoresist, PMMA 950k, is coated on top of the sample using a spin-coater, using 4000 rpm for 60 seconds, and heated again at 180°C for 60 seconds.

Then the sample is placed inside the UV-system, underneath a shadow mask, after which the sample is exposed for 1500 seconds to UV-radiation in hard contact mode, so that a pattern is created. Subsequently, the photoresist that is exposed to the UV-radiation is removed using a LOR/ZEP solution and cleaned afterwards with a MIBK/IPA (1:3) solution. The photoresist that was not exposed will remain. This can for example be used to prevent that by exposure to a plasma in a reactive ion etching system, the graphene will not be etched away. After etching step, the remaining photoresist is removed and a structure of graphene will remain.



Figure 14: A schematic view etching using photoresist and deep-UV photolithography. a) Graphene on top of SiC b) A double layer of photoresist is applied on top of the graphene. c) & d) The sample is exposed to UV-radiation that makes a pattern. e) The sample is developed and the exposed photoresist is removed using a solvent. f) & g) The graphene with no photoresist is etched away by plasma in a reactive ion etching system h) Graphene with structure remains.

### 3.2 Hydrogenation methods

In this thesis we investigated three methods for hydrogenation of graphene. In this section a description of these three methods can be found. Method I consist of exposure to hydrogenplasma, and method II and method III consist of exposure to neutral atomic hydrogen gas, of which the gas of method II is at room temperature and the gas of method III at an elevated temperature.

### 3.2.1 Hydrogenation method I: hydrogen plasma

Hydrogenation of exfoliated graphene can be done in a plasma which consists of a mixture of argon and hydrogen (75 % argon and 25 % hydrogen) in a RIE-system (See Figure 15). This method is the same as described in Reference [42]. Here the plasma is made in the same way as in etching, but with manner kinetic energy as to not 'kick out' the carbon atoms, but with enough energy to overcome the carbon-carbon  $sp^2$  bond, creating a carbon-hydrogen  $sp^3$  bond. The kinetic energy of the hydrogen ions can be changed by changing the DC voltage of the electrodes, between a DC voltage of 0 volt (no acceleration) to a DC voltage of 9 volt. A higher voltage will result in a higher kinetic energy per ion. If the pressure of the gas flow of hydrogen is increased, the hydrogen plasma density will also increase. This leads to a higher hydrogenation rate. However, if the flow is too large, it is more difficult to control the hydrogenation rate.



Figure 15: A schematic view of the hydrogenation proces by a reactive ion-etching plasma. The electromagnetic field accelerates the positive hydrogen ions towards the negative electrode. The shadow mask ensures that only a certain part of the sample is exposed to the hydrogen plasma.

It is possible to selectively expose certain areas on the graphene sample to the hydrogen plasma by using a shadow mask or a resist pattern using photolithography.

#### 3.2.2 Hydrogenation method II: radio frequency atomic hydrogen

The second method for hydrogenation consists of exposure to atomic hydrogen. Hydrogen plasma is made using a RF Field, after which the gas is led through a capilair. Here the wall of the capilair absorbs some of the charge and causes the gas to adopt room temperature. At the end of the capilair a teflon shield blocks and reflects the charged particles, causing only neutral H and  $H_2$  to pass and reach the sample [43]. In this particular setup, the same as in Reference [44], it is possible to perform *in situ* measurements on transport phenomena, so the resistance can be measured as function of exposure time. Figure 16 gives a schematic image of the setup.



Figure 16: A schematic view of hydrogenation by a atomic hydrogen at room temperature. A) A RF-field between the electrodes generates a hydrogen plasma. B) The plasma is led through a capilair and collides with the wall. Through this collisions the plasma adopts the room temperature and loses most of its charge. This results in a mixture of hydrogen ions, atomic hydrogen and  $H_2$  molecules. C) A shield blocks all the charged particles, so that only H and  $H_2$  can reach the sample. In this setup, in situ measurements can be done, while the sample is exposed to the hydrogen beam.

### 3.2.3 Hydrogenation method III: atomic hydrogen by thermal cracking

Another method for creating an atomic hydrogen beam is by thermal cracking of  $H_2$  gas[45] [1]. Here hydrogen gas in high vacuum is heated with a tungsten filament. The  $H_2$ -gas is induced by thermal cracking and the resulting atomic H-gas is led to the device. See Figure 17 for a schematic image of the setup. The temperature of the tungsten filament is between the 1400-1700°C. A higher temperature of the filament will cause a higher kinetic energy of the hydrogen atoms. The hydrogen atoms in the beam should have enough kinetic energy to overcome the activation barrier [46]. A temperature that is too high however will cause the pressure in the system to rise to a too high level. This will complicate the process to fabricate an uniform layer of hydrogenated graphene [46].



Figure 17: A schematic view of exposure to atomic hydrogen.  $H_2$ -gas is led through a capilair with a tungsten filament, which has a temperature of  $1400-1700^{\circ}$  C. Due to the high temperature, the activation barrier for the dissociation of  $H_2$  is overcome and the  $H_2$ -gas is cracked to H-atoms, creating a neutral atomic hydrogen gas.

### 3.3 Scanning probe microscopy

### 3.3.1 Atomic force microscopy

The atomic force microscope (AFM) is a type of scanning probe microscopy, where it is possible to see topographic features of a surface in the subnanometer regime. An AFM consists of a tip on a cantilever, which is brought into vibration using a piezoelectric element and taps on the surface of a sample or device with a certain drive frequency and drive amplitude (Figure 18). When the tips is in close proximity of the surface of the sample, different atomic forces act on the tip and results in a certain deflection of the cantilever. The deflection of the cantilever is measured using a laser spot which is aligned on the cantilever and reflected back into a photodiode. The sample itself is positioned on a scanner, which moves back and forth to make a scan line. Since a different height on a surface result in a different deflection of the cantilever, the topography of the surface is constructed line by line.



Figure 18: A schematic picture of an atomic force microscope

#### 3.3.2 Magnetic force microscopy

The magnetic force microscope (MFM) is a mode of a normal AFM, where a magnetic tip is used instead of a normal tip. The magnetic tip ensures that after a scan not only the topography of a surface is imaged, but also the magnetization of that topography is known. The MFM-technique consists of taking first a scan in tapping mode, like a normal AFM-image. The same scan, the interleave scan, is done again in liftmode. This scan mode uses the height information of the first scan in tapping mode, to koop the distance between the tip and the surface constant. The assumption is made that the minimal distance, calculated using Figure 19, between the tip of the cantilever and the surface of the sample is roughly the same for MFM as calculated in tapping mode.

In lift mode the short range force, which is responsible for the main features in an AFM image, can be neglected and only the long range force, like the magnetic dipole-dipole interaction of the tip and the surface, are imaged. In this way a phase difference image of a certain area can be made. The magnetization of the sample can be changed after a scan. If the scan is done again, an image of a topography with paramagnetic features should be the same. If the sample has ferromagnetic features, that area should have a inversed magnetization after reversing the magnetization of the sample. To be more exact, the ferromagnetic areas will keep absolutely the same magnetization if

a standard background is subtracted, but the sign of the magnetization will now be inversed with respect to the tip of the MFM, whose magnetization was kept the same. This was also measured in Figure 8.

With magnetic force microscopy the tip is kept a constant distance above the surface during the second, magnetic scan (interleave scan). If the height is too low with respect to the drive amplitude, the tip of the cantilever will touch the surface with too much force and the tip will get blunt and the resolution will go down. A force plot in tapping-mode (AFM-mode) can be made to check the minimal height of the tip. This is a plot of the deflection error of the tip versus the distance of the cantilever (Figure 19).

The tip will approach the surface until the cohesive and adhesive forces between the tip and the surface pull the tip down which results in a steep valley, after which the plot will continue linearly. Subsequently, the cantilever is retracted, at point C, which follows the same line to point D. Due to the adhesive and cohesive forces, the valley is less steep and deeper, compared the approach of the tip. The part of the Figure 19 which behaves linearly, from point B to point C, can be used to determine a minimal distance of tip. This is approximately 70 nm.



Figure 19: A forceplot of the AFM, where the tip of the AFM is gradually brought closer to the surface of the sample. The deflection is first constant, till a certain distance between the tip and the surface is reached, at point A. Here the tip is so close to the surface that the adhesive and cohesive forces take over and the tip jumps to the surface, point B. Next is a linear response between deflection of the cantilever and distance to the surface of the sample. This linear response can be used to calculated the minimal distance between the tip and the surface of the sample. The red line is from retracting the cantilever. First it behaves linearly, just as in approach, but since the tip is already at the surface, the adhesive and cohesive forces have a longer effect on the tip, causing that before and after retraction of the tip are not the same (point D).

### 3.4 Raman spectroscopy

Raman spectroscopy is a technique that uses the scattering of light from a laser by atoms to get a spectrum that is unique for every molecule, atom or chemical bond between atoms and is used to determine the kind of material or type of bonds in the material. Atoms scatter the incoming photons in a few ways. Rayleigh scattering, Figure 20a, is elastic scattering where there is no energy exchange between the incoming and transmitted photon. Next, there is Stokes scattering. Here an atom absorbs a photon and goes to a higher virtual state, after which it decays to a lower ground state, and effectively absorbs some of the energy of the photon. Anti-Stokes scattering is the opposite, the atom loses some of its energy after it decays to a higher ground state. Stokes and anti-Stokes scattering (Figure 20b and Figure 20c) cause that the transmitted photon to have a different energy than the energy from the photons of the laser, and are measured as the Raman shift (in cm<sup>-1</sup>). The final output is the Raman spectrum, where the intensity (in arbitrary units) is plotted against the Raman shift .



Figure 20: The energy level diagram of the different states of the scattering processes. A) The elastic Rayleigh scattering, which has a wavelength close to the laser. This type of scattering is filtered out of the deflected beam. B) If the final state of the molecule has more energy than its initial state, a photon is emitted with a lower energy, the Stokes scattering. C) If the final state of the molecule has less energy than its initial state, a photon is emitted with a higher energy, the Anti-Stokes scattering. Image taken from [47]

Figure 21 shows a schematical images of a Raman setup. A laser illuminates the sample, after which the refracted light is led through a monochromator, which filters out all the light with the wavelength of the laser. Finally, the light is collected in a detector, which is used to calculate the Raman spectrum [48].

The Raman spectrum of pristine graphene should have two clear peaks, the G-peak around a Raman shift of 1583  $cm^{-1}$  and the 2D-peak around a Raman shift of 2680  $cm^{-1}$  as can be seen in Figure 22. The G-peak is caused by stretching of the carbon-carbon bond and is always present at graphene. This peak is often used to determain changes in the flat surface through strain of the carbon-carbon  $sp^2$  bond, *e.g.* wrinkling. The D-peak, which will appear around a Raman shift of 1340  $cm^{-1}$ , is affected by distortions in the  $sp^2$  bond. Adatoms or vacancies for instance can be detected around this Raman shift. Since pristine graphene, thus without defects, does not show these distortions, they are not depicted in Figure 22. The 2D-peak is a signature for  $sp^2$  bonds in graphite materials. The ratio between the G- and 2D-peak can be used to determine the number of graphite layers [49].

The spectrum of silicon carbide should be subtracted and if the hydrogenation is successful,



Figure 21: A schematic picture of a Raman setup. The laser illuminates the sample, after which the scattered light is directed through a filter to the detector.



Figure 22: Raman spectrum of pristine graphene with the two most usefull peaks. The G-peak at 1583 cm<sup>-1</sup> represents the strain of sp<sup>2</sup> bonds. The 2D-peak at 2680 cm<sup>-1</sup> is a signature of the carbon-carbon sp<sup>2</sup> bond. Image taken from [49]

the  $sp^2$  bonds will be distorted and a D-peak will appear besides the G-peak and the 2D-peak that are present in pristine graphene.

### 3.5 Transport measurements

#### 3.5.1 Lock-in amplifier

In this section an explanation of the workings of a lock-in amplifier can be found, which we used to perform transport measurements. The lock-in amplifier allows measurements on small AC signals, even if the noise is a thousand times larger than the actual signal. Using the phase-sensitive detection all noise signals different than the reference signal are filtered out [50].

A signal with a fixed frequency origins from the experiment, *i.e.* the electronic and magnetoelectronic measurements. The lock-in amplifier detects this signal with an amplitude  $V_{sig}$ , a freqency at  $\omega_r$  and a phase of  $\theta_{sig}$ . The reference signal can be written as  $V_{sig} \sin(\omega_r t + \theta_{sig})$ . The lock-in amplifiers generate subsequently their own internal reference signal using a phase-lockedloop locked to the external reference signal with an amplitude  $V_L$ , a frequency at  $\omega_L$  and a phase of  $\theta_{ref}$ . The internal reference signal can be written as  $V_L \sin(\omega_L t + \theta_{ref})$ .

The lock-in amplifier amplifies the signal from the experiment and multiplies it with the reference signal using a phase-sensitive detector. The following formula for the output of the phasesensitive detector,  $V_{PSD}$ , the product of the two earlier mentioned formulas, is obtained:

$$V_{PSD} = V_{sig} V_L \sin(\omega_r t + \theta_{sig}) \sin(\omega_L t + \theta_{ref})$$
  
=  $\frac{1}{2} V_{sig} V_L \cos((\omega_r - \omega_L) t + \theta_{sig} - \theta_{ref})$   
-  $\frac{1}{2} V_{sig} V_L \cos((\omega_r + \omega_L) t + \theta_{sig} + \theta_{ref})$  (11)

This output has two AC signals, one at the difference frequency  $\omega_r - \omega_L$  and the other at the sum frequency  $\omega_r + \omega_L$ . If this signal is now led through a low-pass filter, all the AC signals with  $\omega_r \neq \omega_L$  will be removed. If  $\omega_r = \omega_L$ , the difference frequency will be a DC signal, so that the output will not be equal to zero:

$$V_{PSD} = \frac{1}{2} V_{sig} V_L \cos(\theta_{sig} - \theta_{ref})$$
(12)

This is a DC signal proportional to the signal amplitude and enables the lock-in amplifier, if the appropriate filters are used, to detect signals which are a factor 1000 smaller than the present noise.

#### 3.5.2 Electronic measurements

The square resistance or 2D resistivity,  $\rho$ , of exfoliated graphene devices will increase for increasing hydrogen-plasma exposure time[42] due to an decrease of free electrons. An increase in square resistance is thus an indication of successful hydrogenation for exfoliated graphene. It is assumed that this is also the case for epitaxial graphene on SiC.

The square resistance is the resistance of a uniform, thin film of constant thickness, where the resistance only depends on the shape of the film. The resistance can be measured using a '4 probe'-measurement, where the probes are positioned anywhere on the edge of the sample. The 'van der Pauw'-method [51] is used to calculate the square resistance, where there is the relationship:

$$\exp(-\frac{\pi d}{\rho_{3D}}R_{AB,CD}) + \exp(-\frac{\pi d}{\rho_{3D}}R_{BC,DA}) = 1$$
(13)

Here is d the thickness of the thin film,  $\rho_{2D}$  the square resistance and  $R_{AB,CD} = \frac{V_D - C}{I_{AB}}$ . A,B,C and D are here arbitrary contacts at the edge of the device. For graphene, a 2D-material, Formula 13 can be simplified to:

$$e^{-\frac{\pi}{\rho_{2D}}R_{AB,CD}} + e^{-\frac{\pi}{\rho_{2D}}R_{BC,DA}} = 1$$
(14)

The first geometry of the sample consists of a graphene square with at the corners gold contacts (Figure 23a) positioned. This geometry is not ideal, since there are numerous current paths if a voltage or current is applied to two gold contacts. This makes the 'van der Pauw'-method less accurate. A more ideal case for the van der Pauw geometry is a Hall-bar (Figure 23b), which should provide better results.



Figure 23: A schematic image of the 'van der Pauw' geometries. a) Van der Pauw geometry with contacts on the 4 corners of a square. b) A more ideal geometry, a Hall-bar. This configuration is more ideal, since there are less current paths between the different contacts.

### 3.5.3 Magneto-electric measurements

The Hall effect occurs when a magnetic field is applied perpendicular to the direction of an electrical current flow. The magnetic field deflects charge carriers in a material, from their normal current direction. This results in a voltage difference transverse to the current direction. Using Formula 5, the voltage difference can used to calculate the transversal resistance, the Hall-resistance [18]:

$$\rho_{xy} = -\frac{V_{xy}}{i_x x} = -\frac{\omega_c \tau}{\sigma_0} = -\frac{B}{ne} = R_H \tag{15}$$

Since the sp<sup>2</sup> bonds of the graphene will change in  $sp^3$  bonds if hydrogen binds to the carbon, there will be less free electrons. This causes that the carrier density will go down. The carrier density can be measured using the Hall effect.

The slope of the Hall-resistance as function of the magnetic field,  $\frac{\partial R_H}{\partial B}$ , can thus be used to calculate the carrier density or carrier type of a material. Formula 15 becomes:

$$n = \frac{1}{\frac{\partial R_H}{\partial B} \mathbf{e}} \tag{16}$$

A local magnetic moment in the graphene will enhance locally an applied external magnetic field, regardless of the orientation of the field. This will cause that if the Hall resistance is set as function of the applied magnetic field, there will be besides the Hall effect an extra effect. This effect will have a parabolic behaviour and should be stronger for more magnetic moments. If a carbon-hydrogen bond in graphene creates a magnetic moment, this will be visible in the Hall measurements. Also, a longer exposure time will create more magnetic moments in the epitaxial graphene on SiC and the parabolic behavior will be more present. If the magnetic moments are ferromagnetic coupled, some hysteresis effects instead of a parabolic effect will be induced if the Hall-effect is investigated.

### 4 Results

In this chapter, the experimental investigations of three different methods for the hydrogenation of epitaxial graphene on SiC will be presented. Method I consists of the exposure of the graphene to hydrogen plasma, made in a reactive ion etching system. Method II consists of exposure of the graphene to an atomic hydrogen beam at room temperature, made by radio frequency radiation. The last method, Method III, consists of exposure of the graphene to an atomic hydrogen beam of elevated temperature, using thermal cracking of  $H_2$ -gas.

The three methods are investigated using atomic force microscopy and magnetic force microscopy, electronic and magnetoelectric transport measurements, and Raman spectroscopy. See Appendix 6 for the complete overview of the samples and how they were processed.

### 4.1 Hydrogenation Method I: hydrogen plasma

We exposed epitaxial graphene on SiC to a hydrogen plasma, made in a reactive ion etching system, as explained in Section 3.2.1. This is a relatively simple procedure, proven to be succesful for exfoliated graphene [42]. We investigated Method I on three samples with the use of scanning probe measurements and transport measurements, which are explained in Section 3.3.1 and Section 3.5.

#### 4.1.1 Scanning probe microscopy

Figure 24 shows a typical AFM image of epitaxial graphene on SiC. The surface topography images shows the different terraces with patches of bilayer graphene at the terrace edges.





Figure 25 shows the  $15 \times 3.5 \,\mu$ m surface topography image taken after 15 and 75 minutes of exposure to the hydrogen plasma, where a DC voltage of 5 V is applied to the electrodes. We see a surface topography that resembles the unexposed sample, with some bilayer along the terrace edges. No change in surface topography is visible.

Next, we exposed the same sample to a plasma, where the hydrogen ions have a higher kinetic energy. This way we increase the chance of an ion overcoming the energy barrier of the  $sp^2$  bond and form a carbon-hydrogen bond. Figure 26 shows the  $5 \times 5 \mu$ m surface topography image taken after 15 and 75 minutes of exposure, where a DC voltage of 9 V is applied between the electrodes. We see a surface topography with a clear edge and with some bilayer graphene along the terrace edges. The bright spots on Figure 26b are believed to be dirt particles on the graphene sample. Additionally, some structure can be seen on the surface of Figure 26a and Figure 26b (dark traces). The height of the structure is roughly 0.5 nm lower than the rest of the terrace and is not visible in Figure 25 and Figure 24. The visible structure is different than the partly hydrogenated sample



Figure 25: AFM surface topography images of a  $15 \times 3.5 \,\mu$ m graphene area. Both are exposed to a hydrogen plasma made with a DC voltage between the electrodes of 5 V. a) Graphene that is exposed for 15 minuten. b) Graphene that is exposed for in total 75 minuten. Although they are not images of the same area, they both show a typical image of the surface topography.

of Reference[1]. It could be possible that the hydrogenation process elevated almost the complete terrace, except the dark traces, or another process that altered the surface topography, for instance by damaging.



Figure 26: AFM surface topography images of two  $5 \times 5 \,\mu\text{m}$  graphene areas. Both are exposed to a hydrogen plasma made with a DC voltage between the electrodes of 9 V. a) Graphene that is exposed for 15 minutes. b) Graphene that is exposed for 75 minutes in total. Although these are not images of the same area, they both show a typical image of the surface topography of graphene after different exposure times.

#### 4.1.2 Transport measurements

To investigate the Hydrogenation Method I in more detail, we performed electronic and magnetoelectric transport measurements in parallel with the AFM measurements. The transport experiments existed of measuring the resistance and carrier density of the graphene sample. The measurements are done as soon as possible after exposure to the hydrogen plasma, varying between a few minutes and 3 days.

The carrier density is calculated using Equation 15, where the slope of the Hall-resistance in Figure 27a is equal to  $\frac{\partial R}{\partial B}$ . We show here the carrier density of graphene exposed to a hydrogen plasma (made with a voltage of 9 V), for different total exposure times. The results are shown in Figure 27b. The carrier density shows large fluctuations between  $10^{13} - 10^{14} \text{ cm}^{-1}$ , with no clear relation to the exposure time.



Figure 27: a) A typical measurement of the Hall-effect, where the transverse resistance is measured while sweeping the out-of-plane magnetic field from -0.25 T to 0.25 T. The ratio  $\frac{\partial R}{\partial B}$  is equal to the slope of the fitted line in the graph, the red line. b) The square resistance of the graphene as function of the exposure time to the hydrogen plasma, made with a DC voltage of 9 V.

We used the 'van der Pauw'-method, described in Section 3.5.2, to calculate the square resistance. Figure 28a shows the square resistance as function of the exposure time to the hydrogen plasma (9 V). The square resistance shows large fluctuations between 2-17 kΩ, with no clear relation to the exposure time. In Figure 28b we plotted the carrier density as function of the square resistance. We see an increase in  $\rho$  for a higher n, which is is in contradiction with what is expected. An increase in carbon-hydrogen bonds leads to a decrease in  $sp^2$  bonds, decreasing the number of charge carriers which should lead to an increase in the resistance (from kΩ to ~ MΩ).

A possible explanation is that the 'van der Pauw'-equation is valid for undamaged graphene, since epitaxial graphene is heavily n-doped and the measurements were not done near the Dirac point. However, if a hydrogen ion got enough kinetic energy at 9 V to damage parts of the graphene less paths were available for the charge carriers. This makes the transport measurements between two contacts on the graphene less accurate.

Furthermore, in the case of ferromagnetic domains, hysteresis effects should arise in magnetoelectric transport measurements. The Hall-resistance of Figure 27a does not show significant parabolic/hysteresis effects (<1%, level of the noise), so there is probably no ferromagnetism present.

#### 4.1.3 Conclusion

AFM images did show some changes after exposure to the hydrogen plasma, but they were different than the expected changes according to Reference [1]. The transport measurements also showed



Figure 28: a) The carrier density of the graphene as function of the exposure time to the hydrogen plasma, made with an applied DC voltage of 9V. b) The carrier density plotted as function of the square resistance.

some change, but no clear relation to the exposure time was present. The unexpected relation between exposure time and carrier density and the square resistance indicates that the process is partly reversible. If the process is partly reversible, the measurement depends than on the time between exposure and measurement instead on exposure time.

The unexpected relation between the carrier density and the square resistance in Figure 28 could mean that the 'van der Pauw'-method is not valid, perhaps due to damage to the graphene. The first hydrogenation method gives no control over the hydrogenation rate.

Because of the unpredictable, reversible nature of Method I, we also investigated other hydrogenation methods. The second hydrogenation method provides the possibility for *in situ* measurements. The results will be described in the next section.

### 4.2 Hydrogenation Method II: radio frequency atomic hydrogen beam

We exposed epitaxial graphene on SiC to an atomic hydrogen beam at room temperature. The atomic hydrogen beam is made by dissociation of  $H_2$ -gas by exposure to radio frequency radiation, explained in Section 3.2.2. The setup used for this method has the advantage that the hydrogenation process can be investigated in more detail, since it allows for *in situ* transport measurements. One epitaxial graphene sample on SiC with four gold contacts has been exposed for in total 30 hours to the hydrogen gas.

To investigate this hydrogenation method, we performed *in situ* resistance measurements. Afterwards we performed scanning probe microscopy measurements and transport measurements and magnetic hysteresis is investigated using the Hall-effect.

In addition, two samples of graphene were exposed to the atomic hydrogen beam before it was possible to do *in situ* resistance measurements. Transport measurements were done on these samples.

#### 4.2.1 In situ resistance measurements

The *in situ* resistance measurement of the graphene sample is done during exposure for a total of approximately 30 hours. Figure 29a shows the the resistance for the first 4 hours. During these 4 hours the chamber was pumped, the exposure to the atomic hydrogen beam was started and the pressure of the beam was varied.

The remaining 26 hours showed a flat line with no significant changes in resistance, untill the chamber was vented. During venting the chamber, the resistance rose for a few  $100 \Omega$ , which is probably caused by air particles that deposited on the graphene surface.

A constant background of  $2.1 \text{ k}\Omega$ , was subtracted from the measured *in situ* resistance. The background was partly caused by the resistance of the wires and partly from a difference in the ground potential of the voltage meter with respect to the sample chamber.

Figure 29b shows the first 30 minutes of the measurement, during pumping and before exposure. Due to pumping of the chamber containing the graphene sample, present adsorbates are removed by evaporation from the graphene. This leads to a drop of the resistance until it is satured at approximately  $2 k\Omega$ .



Figure 29: a) The resistance of the graphene as function of the total measurement time. b) The resistance as function of the measurement time during pumping.

After 35 minutes, the hydrogen beam is turned on, as described in Section 3.2.3. Figure 30a shows the 40 minutes after starting the exposure to the atomic hydrogen beam. A decrease in resistance is visible, probably due to a change in the pressure of the gas.

Next, after saturation of the resistance, we changed the pressure of the hydrogen gas. A higher pressure for the atomic hydrogen beam results in an increase in atomic hydrogen atoms. This may increase the absorption rate of hydrogen atoms and so an increase in *in situ* resistance. Figure 30b shows the resistance for an increase of the pressure in the plasma chamber during exposure. We changed the pressure of the hydrogen gas from 0.1 mbar (at A in Figure 30b) to 0.3 mbar, 0.6 mbar and eventually to 1.0 mbar (B, C and D respectively). We observed a change in resistance in the order of  $\sim k\Omega$ . After the pressure is set again at (0.1 mbar B in Figure 30b), the resistance decreases again to resistance of 0.1 mbar.



Figure 30: a) The resistance of the graphene as a function of the exposure time, after radio frequency radiation is applied to the hydrogen gas. b) The resistance as function of exposure time at different hydrogen gas pressures. The pressure at A is 0.1 mbar, at B it is 0.3 mbar, at C it is 0.6 mbar and the pressure is at D is 1.0 mbar. At E the pressure is of the hydrogen beam is put back at 0.1 mbar.

An increase in resistance is expected ( $\sim M\Omega$ ) by hydrogenation, but only smaller changes were visible ( $\sim k\Omega$ ). The changes in resistance can be explained by a different chamber pressure, causing a small change in dynamic equilibrium conditions (adsorbing / desorbing rate of hydrogen atoms by the graphene).

#### 4.2.2 Scanning probe measurements

Figure 31a shows the surface topography of the graphene sample after the exposure to the atomic hydrogen beam. The terraces and edges are visible, just as several lighter spots visible. The big, bright spots have a high elevation and are probably caused by dirt particles. The smaller spots in the blue circle have an elevation of 0.8 - 1 nm, as illustrated in the height profile of the AFM image (Figure 31b), which has been taken along the blue line. This elevation is higher than the expected elevation of 0.3 nm found in Reference [1], but the elevation is too low to be caused by dirt particles.

Reference [1] also predicts that carbon-hydrogen bonds create a local ferromagnetic domain. Figure 32a and Figure 32b show the MFM images for a reversed magnetization of the sample. The edges and terraces of the graphene sample are clearly visible. After reversing the magnetization, the phase difference stays the same, which would not be the case if ferromagnetic domains were created.

The atomic force microscopy measurements did reveal some elevated spots on the surface of epitaxial graphene after exposure to the atomic hydrogen beam, in the order of 0.8 - 1.0 nm, which is higher than in Reference [1]. Magnetic force microscopy did not reveal ferromagnetic properties in the graphene.



Figure 31: a) AFM image taken after exposure to a room temperature atomic hydrogen beam. On the surface topography image extra spots are visible. b) A height profile, taken along the blue line in the blue circle, indicates that the spots are  $\approx 1 \text{ nm}$  higher than the rest of the surface.



Figure 32:  $50 \times 50 \,\mu\text{m}$  image of the phase difference of a graphene sample exposed to a room temperature atomic hydrogen beam. The lighter areas are bilayer graphene regions at the edges. The graphene sample of a) has been magnetized by a magnet with a reversed magnetic field with respect to the magnet that magnetized the graphene sample at b).

### 4.2.3 Transport measurements

We performed electronic and magnetoelectric transport measurements a few hours after finishing the exposure to the atomic hydrogen beam. The square resistance was increased to  $\rho = 8.61 \text{ k}\Omega$ . The carrier density was  $n = 1.10 \ 10^{13} \pm 2.23 \ 10^{12} \text{ cm}^{-2}$ .

Figure 33 shows the Hall resistance as function of an external applied magnetic field, which is used to calculate the carrier density. There are no hysteresis effects visible, so we conclude that no ferromagnetic domains are created due to the hydrogenation proces.

Further transport measurement were done on the two samples which were exposed without performing *in situ* resistance measurements. The square resistance of the two samples after exposure is  $\rho = 15.63 \text{ k}\Omega$  and  $\rho = 49.53 \text{ k}\Omega$  and the carrier density is  $n = 4.28 \ 10^{13} \text{ cm}^{-2}$  and  $n = 4.33 \ 10^{13} \text{ cm}^{-2}$ .

The square resistance of the samples is higher after hydrogenation, but it is still orders of magnitude lower than the expected resistance in the order of  $\sim M\Omega$ . The carrier density remained the same as pristine graphene, or increased which is in contradiction with Reference [42]. Probably some kind of adsorbate influences the resistance. No hysteresis effects, which could indicate a ferromagnetic domain, were visible.



Figure 33: Hall resistance of the graphene sample that is exposed for more than 30 hours to an atomic hydrogen beam. The slope used to calculate the carrier density is shown in red. No hysteresis effects are visible and so no ferromagnetism is present.

### 4.2.4 Conclusion

Minor changes were visible in the resistance during the *in situ* measurements, but they can probably all be contributed to changes in the pressure of the chamber. The AFM images did show an elevation, but is was not in the same order as expected according to Reference [1]. The Hall-effect measurement and the magnetic force microscopy measurement did not show signs of any present ferromagnetic domains. Further, the transport measurements did not show the expected changes in resistance or carrier density. We can assume that the second hydrogenation method does not lead to a significant amount of permanent carbon-hydrogen bonds. The samples that have been exposed before the setup was adjusted to perform *in situ* measurements, did show a bigger change in resistance, but it is still minor with respect to the expectations of Reference [42]. The minor changes are probably caused by some adsorbates, perhaps hydrogen, but it does not lead to detectable, significant changes in the surface topography.

Hydrogenation Method II is not a successful method to control the creation rate of carbonhydrogen bonds in epitaxial graphene on SiC. The next section will treat the method of Reference [1], where successful hydrogenation was reported.

### 4.3 Hydrogenation Method III: atomic hydrogen beam by thermal cracking

We exposed epitaxial graphene on SiC to an atomic hydrogen beam, by dissociation of  $H_2$ -gas by thermal cracking, explained in Section 3.2.3. Successful hydrogenation of graphene using this method is reported in Reference [1].

Three samples are investigated using this method. One has been made with Ti/Au contacts to investigate the compatibility of hydrogenation with lithography. The samples were exposed for 3 minutes to a hydrogen beam at a pressure of  $1.7-2\,10^{-6}$  mbar. After exposure, the graphene samples were investigated using scanning probe measurements (AFM and MFM) and Raman spectroscopy.

#### 4.3.1 Scanning probe measurements

Figure 34a shows the  $1 \times 1 \mu m$  surface topography image of a single terrace taken right after 3 minutes of exposure to the atomic hydrogen beam. The slightly darker triangles are formed by a mismatch error in the SiC latice, which is visible in the graphene layer. This has no influence on the hydrogenation process. Slightly brighter spots and larger contiguous areas are also visible (black circle). A height profile of the sample is taken along the line in the blue circle, which is visible in Figure 34b. All the slightly brighter areas have an elevation of approximated 0.2-0.3 nm.



Figure 34: a)1 × 1 µm surface topography image of graphene exposed to an atomic hydrogen beam, made by thermal cracking. The black triangles (in the red circle) are due to a mismatch in the SiC lattice which is also visible in the graphene. The lighter areas (in the black circle) are approximately 0.2 - 0.3 nm higher with the respect to the rest of the surface. The line in the blue circle indicates the place where the height profile of b) is taken. b) Height profile of hydrogenated sample of graphene. The height profile consists of the average height over approximately 100nm along the blue line on the graphene sample. The increase of approximately 0.2 - 0.3

mathrmnm is the same as theory predicts for a successful hydrogenated area.

Figure 35a shows the  $1 \times 1 \mu m$  AFM image of a different sample taken a few minutes after exposure to the atomic hydrogen beam. The larger, brighter areas (blue circle) have an elevation of 0.3 nm, but the smaller, brightest spots (in the black circle) have an elevation of 0.6 nm.

After two weeks, surface topography images were taken again. Figure 35b shows the AFM image, where the darker triangles due to a lattice mismatch are clearly visible. In the top right the terrace edge is visible. The slightly brighter spots and larger, contiguous areas (blue circle) are present to a lesser extent. The elevation of these brighter areas is 0.3 nm, but an elevation is not present at the terrace edge, probably due to the bilayer graphene.

After six weeks, the exposed sample is investigated again with AFM. Figure 36a is the  $5 \times 5$  mum surface topography image, with the terraces and edges are clearly visible, as well as some bilayer



Figure 35: a)  $1 \times 1 \mu m$  surface topography image, taken minutes after exposure to the atomic hydrogen beam. The bigger, lighter areas have an elevation of approximately 0.3 nm and the bright, white spots an elevation of approximation 0.7 nm. b)  $5 \times 5 \mu m$  surface topography image near a terrace edge, taken 2 weeks after exposure to the atomic hydrogen beam. The darker triangles are caused by an lowering due to a lattice mismatch. In the blue circle an elevation is shown of approximately 0.3 nm. Near the terrace edge above the blue circle some bilayer graphene is visible. There is no extra elevation due to hydrogen atoms persent.

areas near the edges. The bright spots visible have an elevation of approximately 1 nm, but the height difference of the larger, brighter area inside the blue circle is approximate 0.3 nm.

Figure 36b shows the surface topography image of  $1 \times 1 \mu m$ , taken 6 weeks after the exposure to the atomic hydrogen beam. The edge and 2 terraces are clearly visible. There are numerous bright spots of which the brightest spots, inside the white circle, have an elevation of 2 nm. The slightly brighter spots, inside the blue circle, have an elevation of 0.3 nm.



Figure 36: AFM images taken 6 weeks after exposure. a)  $5 \times 5 \,\mu\text{m}$  surface topography image. The different terraces and edges are clearly visible. The bright spots on the graphene have an elevation of approximately 2 nm. b) The  $1 \times 1 \,\mu\text{m}$  surface topography image, taken after 6 weeks. The bright spot in the white circle has an elevation of 1 nm and the bright spot inside the blue circle have an elevation of 0.3 nm.

A week after the exposure MFM measurements were done. The magnetization of the sample is reversed after the first image was taken and the measurement was done again at the same region. Figure 37a and Figure 37b show the surface topography of the sample for the 2 magnetizations.

Different terraces and edges are clearly visible. The two images of the magnetic phase, Figure 37c and Figure 37d, show a clear phase difference between the edges and the terraces, which should always be visible due to the bilayer areas. We see however no reversion in phase difference, if the magnetization is reversed, while reversion due to ferromagnetism should be visible using this scale.



Figure 37: Graphene sample that is exposed to hydrogen for 3 minutes. The magnetization of the tip has been reversed for (b) and (d) with respect to (a) and (c). (a) and (b) are the surface topography images taken using AFM. The different terraces and edges can clearly be seen on these images. (c) and (d) are the phase difference images taken using MFM. Some phase difference can be seen between different terraces, but the phase difference is the same if the magnetization is reversed.

### 4.3.2 Raman spectroscopy

In addition to the scanning probe measurements, Raman spectroscopy is performed to investigate if  $sp^2$  carbon-carbon bonds are distorted. Distortions in the  $sp^2$  bonds are an indication that hydrogen has successfully bonded to the graphene. Such distortions will result in a D-peak at 1340 cm<sup>-1</sup>, besides the present G-peak and 2D-peak, which indicate graphene stretching and carbon graphite layers. See for more details Section 3.4.

Figure 38a shows the Raman spectrum taken a few minutes after exposure. The G- and 2D-peak are clearly present. The D-peak is visible at  $1340 \text{ cm}^{-1}$ . After 2 months, the Raman spectrum was taken again and Figure 38b was obtained. The intensity of the 2D-peak is much lower due to a different alignment of the laser on the sample surface, but this does not influence the presence of the D-peak. The G- and D-peak are also both visible. The intensity ratio of the D- and the G-peak decreased, which indicates that there are less carbon-carbon distortions present in the graphene.



Figure 38: a) Raman spectrum after 3 minutes of exposure to a hydrogen beam, made with a thermal hydrogen cracker. The Raman spectrum is taken minutes after hydrogenation. b) Raman spectrum after 3 minutes of exposure to an atomic hydrogen beam, made with the thermal hydrogen cracker. The Raman spectrum is taken 2 months after hydrogenation. The D-peak, G-peak and 2D-peak can be seen at both plots.

### 4.3.3 Conclusion

We observed an elevation of 0.3 nm on the surface topography images and a D-peak on the Raman spectrum after exposure, which agrees with Reference [1] that the hydrogenation process was successful and carbon-hydrogen bonds are created. However, the brighter areas and the intensity ratio of the D- and the G-peak decreased over time. This is an indication that some of the carbon-hydrogen bonds are gone over time and that the hydrogenation process is reversible. A reversible process can be explained by the fact that a percentage of the coverage can be contributed to hydrogen atoms who bind by physisorption instead of chemisorption to the graphene.

Furthermore, the MFM images did not show change in magnetic phase after reversing the magnetization of the sample. It is not known if they were not present because they can not be created by carbon-hydrogen bonds or if they were gone, since the carbon-hydrogen bonds were gone over time.

Since the hydrogen coverage is still partly present over time, this process seems to be promising to bind hydrogen to graphene. In contradiction with Reference [1] no ferromagnetic domains were observed. More research is needed to identify all parameters for the measurement setup to create only hydrogen coverage by chemisorption and to know how ferromagnetic domains are created.

### 5 Conclusion

### 5.1 Conclusion

This thesis treated three different experimental methods to hydrogenate epitaxial graphene on SiC with the aim to introduce ferromagnetic domains in the graphene. Here the main conclusions of the thesis are summarized.

#### 5.1.1 Hydrogenation by Hydrogen Plasma

The first experimental hydrogenation method was the exposure of epitaxial graphene on SiC to hydrogen plasma. The hydrogen plasma was made in a reactive ion etching system (RIE), explained in Section 3.2.1, and different voltages were applied to make the plasma in the RIE.

We observed a change in the surface topography of the graphene after exposure to the hydrogen plasma. The changes caused a different elevation than expected for graphene, so the change is probably caused by other adsorbants or damage to the graphene.

The transport measurements showed no clear relation between the carrier density and square resistance with respect to the exposure time. The present changes were also much smaller than expected ( $\sim k\Omega$  instead of  $\sim M\Omega$ ). This suggests that the process is probably partly reversible. The measurement depends than on the time between exposure and measurement instead on the exposure time.

Hysteresis effects due to ferromagnetic domains were also not detected during the magnetoelectronic experiments, which indicates that no ferromagnetic domains were present in the graphene.

These observations combined suggests that covalent carbon-hydrogen bonds are not formed, unlike what has been observed previously for exfoliated graphene. This indicates that the hydrogenation process of epitaxial graphene is different from the hydrogenation process of exfoliated graphene, which is probably caused by the presence of a bufferlayer for epitaxial graphene on SiC.

### 5.1.2 Hydrogenation by Atomic Room Temperature Hydrogen Gas

The second experimental hydrogenation method was the exposure of epitaxial graphene on SiC to a room temperature atomic hydrogen beam, which was made using radio frequency radiation, which is explained in Section 3.2.2.

The *in situ* measurements done during exposure and the transport measurements done after exposure did not produce the expected increase in resistance (from  $\sim k\Omega$  to  $\sim M\Omega$ ). The change in surface topography expected for a hydrogenated graphene sample was also not visible after exposure. The small changes that were measured can probably all be contributed to other effects than successful hydrogenation.

In situ measurements provide a good tool to measure the effect of hydrogenation on graphene in real time. This method will provide perhaps better results if the atomic hydrogen beam is heated up. This will increase the energy of the hydrogen atoms, maybe it is than possible to overcome the energy barrier of  $sp^2$  bonds of the carbon in the graphene. It will be more likely that the graphene becomes hydrogenated.

#### 5.1.3 Hydrogenation by Atomic Hydrogen Gas by a Thermal Cracker

The third experimental hydrogenation method was the exposure of epitaxial graphene on SiC to an atomic hydrogen beam of elevated temperature, which was made using thermal cracking, which is explained in Section 3.2.3. This is the same method as is used in Reference [1], where the first evidence for ferromagnetism in epitaxial graphene on SiC was reported.

The AFM-images together with the Raman spectrum of the hydrogenated graphene show some structure of an elevated area (~ 2-3 Å) after exposure to the atomic hydrogen beam and a distortion in carbon-carbon  $sp^2$  bonds, which agrees with Reference [1] for successful hydrogenation. However, the scanning probe images and Raman spectrum taken weeks after exposure to the

atomic hydrogen beam show a decrease in signs for successful hydrogenation. This suggests that the hydrogenation proces is not stable and reversible over time.

No signs of ferromagnetic domains due to the hydrogenation process were measured using MFM measurements. This measurement is done a week after exposure, so it is possible that the ferromagnetic properties are also reversible over time. The exact conditions needed to induce ferromagnetism in epitaxial graphene on SiC are unknown. Reference [1] claims that a bufferlayer and carbon-hydrogen bonds should be present, but perhaps a certain coverage is needed to create the ferromagnetic domains. The carbon-hydrogen bonds have dissociated over time from the graphene layer, decreasing the coverage to such a low level that ferromagnetism could not be detected.

### 5.2 Overall Conclusion and Prospects

The hydrogenation processes were not successful in making the carbon-hydrogen bonds on the epitaxial graphene samples permanent. Some changes were visible but were minor with respect to the expectations of full hydrogen coverage (Method I and Method II) and the process that created carbon-hydrogen bonds were subject to some reversible process (Method III), decreasing the amount of carbon-hydrogen bonds over time. If the parameters for the last method are optimized, for instance the pressure and temperature of the atomic hydrogen beam, the carbon-hydrogen bonds will perhaps become permanent.

MFM measurements done on the sample that showed carbon-hydrogen bonds, but no signs of ferromagnetic domains due to the hydrogenation process were detected. Further research could combine the *in situ* measurements and an atomic hydrogen beam of a higher temperature and the appropriate pressure to increase the chance of successful hydrogenation. After a successful hydrogenation step, the ferromagnetic properties can be investigated, also by checking the influence of time and so the possibility of reversible processes on the ferromagnetic properties. Superconducting quantum interference device (SQUID) measurements can be done in addition to get a more exact measurement on the magnetic properties.

If the parameters are known for successful hydrogenation of epitaxial graphene on sillicon carbide and the creation of ferromagnetic domains, further research can focus on selectively hydrogenate samples, for instance by using shadow masks. These local hydrogenated areas on graphene will induce local ferromagnetic effects. The effect of such a local ferromagnetic area on spin transport can be measured in spintronic devices like the non-local spin valve. Since measurements on spin transport need a small device, the hydrogenation process should be compatible with lithography processes, like photolithography or EBL. Ultimately, local ferromagnetic areas in graphene can used as ferromagnetic contacts, preventing the use of tunnel barrier and a ferromagnetic of a different material.

### 6 Acknowledgments

I must thank a lot people for their help and support for making this masterthesis. I owe my thanks especially to my supervisor Jasper van den Berg, for introducing me to the material graphene and device fabrication, helping me with the experiments and the fact that he was always available to answer questions or explain certain encountered physical phenomena.

My thanks also goes to professor Bart van Wees, group leader of the Physics of Nanodevices group, for giving me the opportunity to work with graphene, which is an very interesting material with numerous interesting properties.

Also I like to thank Ivan Vera Marun, Magda Wojtaszek, Alexey Kaverzin and Eek Huisman from the group Physics of Nanodevices for their suggestions, input and help with the experiments.

Furthermore, I must thank Geert Reitsma and professor Ronnie Hoekstra from the Kernfysisch Versneller Instituut for opportunity to use their setup to expose my samples to atomic hydrogen, hydrogenation method II, and their time and assistance.

Also I owe my thanks to the people from the University of Eindhoven, Ameneh Najafi and professor Cees Flipse, for the opportunity to use their setup to investigate hydrogenation method III, the same as used for Reference [1]. In addition, they gave my lots of possible explanations for the measured phenomena.

I must further thank Erwin Bodewits, Rositza Yakimova, Felix Fromm and Thomas Seyller for providing the epitaxial graphene samples on sillicon carbide.

Finally I must thank professor Ronnie Hoekstra again for taking the time to read the masterthesis and being the co referent.

### References

- A. J. M. Giesbers, K. Uhlirova, M. Konecny, E. C. Peters, M. Burghard, J. Aarts and C. F. J. Flipse, "Interface-Induced Room-Temperature Ferromagnetism in Hydrogenated Epitaxial Graphene", *PHYSICAL REVIEW LETTERS*, vol. 111, OCT 16 2013.
- [2] K. Novoselov, A. Geim, S. Morozov, D. Jiang, Y. Zhang, S. Dubonos, I. Grigorieva and A. Firsov, "Electric field effect in atomically thin carbon films", *SCIENCE*, vol. 306, pp. 666–669, OCT 22 2004.
- [3] T. Maassen, Electron Spin Transport in Graphene-Based Devices. PhD thesis, University of Groningen, Groningen, May 2013.
- [4] C. Lee, X. Wei, J. W. Kysar and J. Hone, "Measurement of the elastic properties and intrinsic strength of monolayer graphene", SCIENCE, vol. 321, pp. 385–388, JUL 18 2008.
- [5] C. for Physics of the Royal Swedish Academy of Sciences, "Scientific Background on the Nobel Prize in Physics 2010: Graphene". OCT 5 2010.
- [6] F. Kusmartsev, W. Wu, M. Pierpoint and K. Yung, "Application of Graphene within Optoelectronic Devices and Transistors", JUN 03 2014.
- [7] J. S. Bunch, S. S. Verbridge, J. S. Alden, A. M. van der Zande, J. M. Parpia, H. G. Craighead and P. L. McEuen, "Impermeable atomic membranes from graphene sheets", *NANO LETTERS*, vol. 8, pp. 2458–2462, AUG 2008.
- [8] T. Maassen, J. J. van den Berg, E. H. Huisman, H. Dijkstra, F. Fromm, T. Seyller and B. J. van Wees, "Localized States Influence Spin Transport in Epitaxial Graphene", *PHYSICAL REVIEW LETTERS*, vol. 110, FEB 6 2013.
- [9] K. M. McCreary, A. G. Swartz, W. Han, J. Fabian and R. K. Kawakami, "Magnetic moment formation in graphene detected by scattering of pure spin currents", *Phys. Rev. Lett.*, vol. 109, p. 186604, Nov 2012.
- [10] L. Xie, X. Wang, J. Lu, Z. Ni, Z. Luo, H. Mao, R. Wang, Y. Wang, H. Huang, D. Qi, R. Liu, T. Yu, Z. Shen, T. Wu, H. Peng, B. Oezyilmaz, K. Loh, A. T. S. Wee, Ariando and W. Chen, "Room temperature ferromagnetism in partially hydrogenated epitaxial graphene", *APPLIED PHYSICS LETTERS*, vol. 98, MAY 9 2011.
- [11] A. K. Geim and K. S. Novoselov, "The rise of graphene", NATURE MATERIALS, vol. 6, pp. 183–191, MAR 2007.
- [12] C. Schonenberger, "Bandstructure of Graphene and Carbon Nanotubes: An Exercise in Condensed Matter Physics". 2000.
- [13] R. Heyrovska, "Atomic structures of graphene, benzene and methane with bond lengths as sums of the single, double and resonance bond radii of carbon", 2008.
- [14] P. R. Wallace, "The band theory of graphite", Phys. Rev., vol. 71, pp. 622–634, May 1947.
- [15] T. Ando, "The electronic properties of graphene and carbon nanotubes", NPG Asia Mater, vol. 1, OCT 21 2009.
- [16] J. C. Charlier, P. C. Eklund, J. Zhu and A. C. Ferrari, "Electron and Phonon Properties of Graphene: Their Relationship with Carbon Nanotubes", in *Carbon Nanotubes*, vol. 111 of *Topics in Applied Physics*, ch. 21, pp. 673–709, Berlin, Heidelberg: Springer Berlin / Heidelberg, 2008.
- [17] E. McCann, K. Kechedzhi, V. I. Fal'ko, H. Suzuura, T. Ando and B. L. Altshuler, "Weak-localization magnetoresistance and valley symmetry in graphene", *Phys. Rev. Lett.*, vol. 97, p. 146805, Oct 2006.
- [18] S. A. L. Avila, Magnetotransport Characterization of Epitaxial Graphene on SiC. PhD thesis, Chalmers University of Technology, Gothenburg, 2012.
- [19] P. T. B. Shaffer, "A review of the structure of silicon carbide", Acta Crystallographica Section B, vol. 25, pp. 477–488, Mar 1969.
- [20] N. Srivastava, G. He, Luxmi, P. C. Mende, R. M. Feenstra and Y. Sun, "Graphene formed on sic under various environments: comparison of si-face and c-face", *Journal of Physics D: Applied Physics*, vol. 45, no. 15, p. 154001, 2012.
- [21] D. e. Gaskill, "Epitaxial Graphene Growth on SiC Wafers".
- [22] W. A. de Heer, C. Berger, M. Ruan, M. Sprinkle, X. Li, Y. Hu, B. Zhang, J. Hankinson and E. Conrad, "Large area and structured epitaxial graphene produced by confinement controlled sublimation of silicon carbide.", Proc Natl Acad Sci U S A, vol. 108, no. 41, pp. 16900–5, 2011.

- [23] U. Starke, S. Forti, K. V. Emtsev and C. Coletti, "Engineering the electronic structure of epitaxial graphene by transfer doping and atomic intercalation", MRS BULLETIN, vol. 37, pp. 1177–1186, DEC 2012.
- [24] T. Seyller, "Electronic properties of SiC surfaces and interfaces: some fundamental and technological aspects", APPLIED PHYSICS A-MATERIALS SCIENCE & PROCESSING, vol. 85, pp. 371–385, DEC 2006.
- [25] C. Virojanadara, M. Syväjarvi, R. Yakimova, L. I. Johansson, A. A. Zakharov and T. Balasubramanian, "Homogeneous large-area graphene layer growth on jspan class="aps-inline-formula"; jmath display="inline"; jmn; 6j/mn; jmi; hj/mi; j/math; j/span; -sic(0001)", Phys. Rev. B, vol. 78, p. 245403, Dec 2008.
- [26] C. Riedl, C. Coletti and U. Starke, "Structural and electronic properties of epitaxial graphene on sic(0001): a review of growth, characterization, transfer doping and hydrogen intercalation", *Journal* of Physics D: Applied Physics, vol. 43, no. 37, p. 374009, 2010.
- [27] M. Sepioni, R. R. Nair, S. Rablen, J. Narayanan, F. Tuna, R. Winpenny, A. K. Geim and I. V. Grigorieva, "Limits on intrinsic magnetism in graphene", *Phys. Rev. Lett.*, vol. 105, p. 207205, Nov 2010.
- [28] J.-H. Chen, W. G. Cullen, C. Jang, M. S. Fuhrer and E. D. Williams, "Defect Scattering in Graphene", *PHYSICAL REVIEW LETTERS*, vol. 102, JUN 12 2009.
- [29] J.-H. Chen, L. Li, W. G. Cullen, E. D. Williams and M. S. Fuhrer, "Tunable Kondo effect in graphene with defects", NATURE PHYSICS, vol. 7, pp. 535–538, JUL 2011.
- [30] Z. Ao and S. Li, *Graphene Simulation*. 2011.
- [31] J. O. Sofo, A. S. Chaudhari and G. D. Barber, "Graphane: A two-dimensional hydrocarbon", PHYS-ICAL REVIEW B, vol. 75, APR 2007.
- [32] I. L. Aleiner and K. B. Efetov, "Effect of disorder on transport in graphene", Phys. Rev. Lett., vol. 97, p. 236801, Dec 2006.
- [33] T. O. Wehling, M. I. Katsnelson and A. I. Lichtenstein, "Adsorbates on graphene: Impurity states and electron scattering", CHEMICAL PHYSICS LETTERS, vol. 476, pp. 125–134, JUL 16 2009.
- [34] R. R. Nair, M. Sepioni, I.-L. Tsai, O. Lehtinen, J. Keinonen, A. V. Krasheninnikov, T. Thomson, A. K. Geim and I. V. Grigorieva, "Spin-half paramagnetism in graphene induced by point defects", *NATURE PHYSICS*, vol. 8, pp. 199–202, MAR 2012.
- [35] C. Riedl, C. Coletti, T. Iwasaki, A. A. Zakharov and U. Starke, "Quasi-free-standing epitaxial graphene on sic obtained by hydrogen intercalation", *Phys. Rev. Lett.*, vol. 103, p. 246804, Dec 2009.
- [36] D. C. Elias, R. R. Nair, T. M. G. Mohiuddin, S. V. Morozov, P. Blake, M. P. Halsall, A. C. Ferrari, D. W. Boukhvalov, M. I. Katsnelson, A. K. Geim and K. S. Novoselov, "Control of Graphene's Properties by Reversible Hydrogenation: Evidence for Graphane", *SCIENCE*, vol. 323, pp. 610–613, JAN 30 2009.
- [37] M. Scheffler, D. Haberer, L. Petaccia, M. Farjam, R. Schlegel, D. Baumann, T. Haenke, A. Grueneis, M. Knupfer, C. Hess and B. Buechner, "Probing Local Hydrogen Impurities in Quasi-Free-Standing Graphene", ACS NANO, vol. 6, pp. 10590–10597, DEC 2012.
- [38] T. Maassen, I. J. Vera-Marun, M. H. D. Guimarães and B. J. van Wees, "Contact-induced spin relaxation in hanle spin precession measurements", *Phys. Rev. B*, vol. 86, p. 235408, Dec 2012.
- [39] E. Wohlfarth, Ferromagnetic materials. 1982.
- [40] A. T. F. J. J. A. B. B. J. v. W. F. J. Jedema, H. B. Heersche, "Electrical detection of spin precession in a metallic mesoscopic spin valve", *Nature*, no. 6882, p. 713716, 2002.
- [41] N. Tombros, Electron Spin Transport in Graphene and Carbon Nanotubes. PhD thesis, University of Groningen, Groningen, 2008.
- [42] M. Wojtaszek, N. Tombros, A. Caretta, P. H. M. van Loosdrecht and B. J. van Wees, "A road to hydrogenating graphene by a reactive ion etching plasma", *JOURNAL OF APPLIED PHYSICS*, vol. 110, SEP 15 2011.
- [43] J. SLEVIN and W. STIRLING, "RADIO-FREQUENCY ATOMIC-HYDROGEN BEAM SOURCE", REVIEW OF SCIENTIFIC INSTRUMENTS, vol. 52, no. 11, pp. 1780–1782, 1981.

- [44] F. Bliek, G. Woestenenk, R. Hoekstra and R. Morgenstern, "State-selective electron-capture measurements for N4+-H and N4+-H-2 collisions", *PHYSICAL REVIEW A*, vol. 57, pp. 221–226, JAN 1998.
- [45] "Atomic hydrogen blowtorch", Feb. 2014.
- [46] U. BISCHLER and E. BERTEL, "SIMPLE SOURCE OF ATOMIC-HYDROGEN FOR ULTRAHIGH-VACUUM APPLICATIONS", JOURNAL OF VACUUM SCIENCE & TECHNOL-OGY A-VACUUM SURFACES AND FILMS, vol. 11, pp. 458–460, MAR-APR 1993.
- [47] Q. H. Xu Yuntao, "Raman: Application", Jan. 2014.
- [48] F. Fromm, M. H. Oliveira, Jr., A. Molina-Sanchez, M. Hundhausen, J. M. J. Lopes, H. Riechert, L. Wirtz and T. Seyller, "Contribution of the buffer layer to the Raman spectrum of epitaxial graphene on SiC(0001)", NEW JOURNAL OF PHYSICS, vol. 15, APR 18 2013.
- [49] Z. Yan and A. Barron, "Characterization of graphene by raman spectroscopy", Jan. 2014.
- [50] "About Lock-In Amplifiers Application Note #3,".
- [51] L. Van der Pauw, "A method of measuring specific resistivity and Hall effect of discs of arbitrary shape", *Philips Technical Review*, vol. 20, 1958.

Name	Proces/Measurement	Date	Comments
Sample	Transport Measurements	21-05-2013	Hydrogenation Method II was investigated.
'C'	Transport Measurements	23-05-2013	Transport measurements revealed changes,
	Transport Measurements (Casimir)	28-05-2013	but they were minor compared the expectations.
	Spincoating, UV and etching	19-09-2013	
	SEM	19-09-2013	
Sample	Transport Measurements	21-05-2013	Hydrogenation Method II was investigated.
'D'	Transport Measurements	23-05-2013	Transport measurements revealed changes,
	Transport Measurements (Casimir)	28-05-2013	but they were minor compared the expectations.
	Spincoating, UV and etching	19-09-2013	
	SEM	19-09-2013	
S17C	E-Beam Evaporation (Ti/Au)	10-06-2013	Hydrogenation Method I was investigated.
	Transport Measurements (Casimir)	11-06-2013	The transport measurements revealed changes,
	AFM/MFM	18-06-2013	but the did not show a clear relation with respect
	Hydrogen Plasma Exposure (RIE)	19-06-2013	to the exposure time. Thereby, the changes in
	Transport Measurements (Dirac)	19-06-2013	the transport measurements were minor compared
	Hydrogen Plasma Exposure (RIE)	20-06-2013	the expectations and showed unexpected behavior.
	Transport Measurements (Dirac)	20-06-2013	Some structure was visible on the AFM-images.
	Transport Measurements (Dirac)	24-06-2013	but they were different than the images with
	Hydrogen Plasma Exposure (RIE)	25-06-2013	hydrogenated epitaxial graphene. Further, no ferro-
	Transport Measurements (Dirac)	26-06-2013	magnetic behavior was detected during the magneto-
	Hydrogen Plasma Exposure (RIE)	28-06-2013	electric measurements. The Raman spectrum of the
	Transport Measurements (Dirac)	01-07-2013	exposed sample could not be used, since the Raman-
	Hydrogen Plasma Exposure (RIE)	01-07-2013	setup was not properly calibrated.
	MFM	08-07-2013	The second se
	Hydrogen Plasma Exposure (RIE)	08-07-2013	-
	MFM	09-07-2013	-
	Hydrogen Plasma Exposure (RIE)	10-07-2013	-
	Transport Measurements (Casimir)	10-07-2013	-
	Hydrogen Plasma Exposure (RIE)	11-07-2013	
	Transport Measurements (Casimir)	11-07-2013	
	Hydrogen Plasma Exposure (RIE)	12-07-2013	
	Transport Measurements (Casimir)	12-07-2013	
	Hydrogen Plasma Exposure (RIE)	15-07-2013	
	MFM	15-07-2013	
	Hydrogen Plasma Exposure (RIE)	14-08-2013	
	Transport Measurement (Casimir)	15-08-2013	
	Hydrogen Plasma Exposure (RIE)	16-08-2013	
	Transport Measurement (Casimir)	16-08-2013	
	Transport Measurement (Casimir)	19-08-2013	
	Hydrogen Plasma Exposure (RIE)	21-08-2013	
	AFM	22-08-2013	
	Hydrogen Plasma Exposure (RIE)	10-09-2013	
	Transport Measurements (Dirac)	10-09-2013	
	Raman spectroscopy	13-11-2013	
S17D	E-Beam evaporation(Ti/Au)	09-07-2013	An attempt has been done to manufacture a flip-
	Flip-chip top gate	23-08-2013	chip top gate, but it has not been successful.
	Transport Measurement (Dirac)	23-08-2013	
	Flip-chip top gate	30-08-2013	
	Transport Measurement (Casimir)	02-09-2013	
	Flip-chip top gate	03-09-2013	
	Transport Measurement	03-09-2013	
S17F	Optical lithography and developing	17-09-2013	

# Appendix A: Sample processing

Name	Proces/Measurement	Date	Comments
S17G	E-Beam evaporation(Ti/Au)	17-09-2013	Hydrogenation Method III was investigated.
	Transport Measurement	30-09-2013	Initially, some change in the surface topography
	H2-Exposure (3 min.)	30-09-2013	were present, as well as carbon-carbon distortions
	MFM	04-10-2013	in the Raman spectrum. They however seemed to
	Raman	13-11-2013	decrease over time.
	SEM	19-11-2013	
	Transport Measurements	19-11-2013	-
	Hydrogen Plasma Exposure (RIE)	26-11-2013	-
	Transport Measurements	26-11-2013	-
	Transport Measurements	26-11-2013	-
	Transport Measurements (Casimir)	28-11-2013	
	Transport Measurements (Casimir)	29-11-2013	
	Raman	19-11-2013	
S17H	Optical lithography and developing	17-09-2013	Hydrogenation Method III was investigated
51111	H2-Exposure (3 min )	30-09-2013	The Raman-setup turned out to be not
	Raman	$12\ 11\ 2013$	properly calibrated
	H2 Exposure (3 min)	12 - 11 - 2013 02 12 2013	property cambrated.
S18A	Hall Bar O2 otching (BIF)	17 00 2013	Hydrogenetics Method II was investigated
JIOA	<b>E</b> Ream exponentian $(Ti / Au)$	17-09-2013	During emposure in gity measurements were done
	H2 Eurosumo	16-09-2013	but did not show the expected increase in resig
	H2-Exposure	24-09-2013	tonce. The transport measurements done often
	Trange out Massurements (Casimin)	01-10-2013 01 10 2012	tance. The transport measurements done after-
	MEM	01-10-2013	wards, did not reveal the expected changes. MFM
	MF M Demonstra	31-10-2013 12 11 2012	and the magnetoelectric measurements did not
0104	Raman	13-11-2013	reveal terromagnetic domains after exposure.
SI9A	Hall-Bar O2-etching (RIE)	27-11-2013	Hydrogenation Method III was investigated.
	E-Beam evaporation (T1/Au))	27-11-2013	The Raman spectrum done after exposure revealed
	Transport Measurements (Casimir)	28-11-2013	the presence of carbon-carbond distortions. The
	Transport Measurements (Casimir)	29-11-2013	surface topography images revealed the expected
	H2-Exposure (3 min.)	03-12-2013	elevations, but were present in a less amount on
	Raman	03-12-2013	later surface topography images.
	AFM	03-12-2013	-
0.221	AFM	06-01-2014	
SEind1	H2-Exposure (3 min.)	30-09-2013	Hydrogenation Method III was investigated.
	MFM	02-10-2013	The surface topography images and Raman spectrum
	MFM	03-10-2013	taken a few minutes after exposure did show elevations
	MF'M	04-10-2013	and carbon-carbon distortions. These indications were
	MFM	07-10-2013	less present when the measurements were done again
	MFM	08-10-2013	a few weeks later. The MFM measurements did not
	Raman	14-10-2013	reveal ferromagnetic domains in the hydrogenated
	MF'M	30-10-2013	graphene.
	AFM	07-11-2013	
	Raman	13-11-2013	
	Raman	02-12-2013	
SEind2	H2-Exposure (3 min.)	02-12-2013	Hydrogenation Method III was investigated.
(GA28)	Raman	02-12-2013	The surface topography images and Raman spectrum
	AFM	02-12-2013	taken a few minutes after exposure did show elevations
	AFM	06-12-2013	and carbon-carbon distortions. These indications were
	Raman	10-12-2013	less present when the measurements were done again
	AFM	10-12-2013	a few weeks later. The MFM measurements did not
	AFM	11-12-2013	reveal ferromagnetic domains in the hydrogenated
	MFM	12-12-2013	graphene.
	MFM	15-12-2013	
	AFM	17-12-2013	
	AFM	18-12-2013	