

hBN-assisted dry transfer of CVD graphene

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Abstract

Graphene, this two-dimensional network composed of carbon arranged in hexagons, attracts more and more interests since the highlight of its incredible properties in 2004 by the group of Novoselov and Geim. Indeed, graphene has shown outstanding thermal and electronic conductivity and great mechanical resistance. This electronic conductivity promises the utilization of graphene in a wide range of applications in nanoscale devices like transistors, Li-ion batteries, supercapacitors, solar cells, etc.

Nevertheless, the integration of graphene in an electronic device requires to place it on an insulator substrate. This work proposes a method to transfer graphene grown by chemical vapor deposition on a copper substrate with the assistance of hexagonal Boron Nitride (hBN). This document analyzes the importance of several parameters (temperature and mechanical pressure during transfer, distance between graphene and hBN flakes at contact, etc.) that influence the smooth functioning of this dry transfer technique.

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Abbreviations

Here follows a brief summary of the main abbreviations present in this work:

AFM	Atomic Force Microscope
BLG	Bilayer Graphene
CNP	Charge Neutrality Point
CVD	Chemical Vapor Deposition
DCB	Double Cantilever Beam
DFT	Density Functional Theory
EXF	Exfoliation
FLG	Few-Layer Graphene
FWHM	Full Width at Half Maximum
Gr	Graphene
hBN	hexagonal Boron Nitride
HOPG	Highly Oriented Pyrolytic Graphite
HPM	Hot Press Machine
LPCVD	Low Pressure Chemical Vapor Deposition
MD	Molecular Dynamics
MET	Mechano-Electro-Thermal
PDMS	Poly-dimethylsiloxane
PECVD	Plasma Enhanced Chemical Vapor Deposition
PMGI	Polymethylglutarimide
PMMA	Polymethyl methacrylate
PPC	PolyPropylene Carbonate
PS	PolyStyrene
PVA	Polyvinyl Alcohol
Rpm	Revolution per minute
SLG	Single Layer Graphene
T_g	Glass transition temperature
TRT	Thermal Release Tape

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Introduction

Graphene is a two-dimensional carbon compound with a hexagonal lattice that shows incredible electronic properties. It is considered promising in a wide range of applications in nanoscale devices like transistors, Li-ion batteries, supercapacitors, solar cells, etc. Significant progress has been realized concerning the synthesis process in order to improve the quality related to the carrier charge mobility. Values like $25\,000\text{ cm}^2/\text{Vs}$ for graphene on a typical insulator substrate of SiO_2 can be found in the literature. A straightforward way to improve the mobility is to use either a smoother insulator underlying substrate or a cleanest transfer process.

One of the main protagonist for this insulator underlying substrate, and the one chosen for this work, is the hexagonal Boron Nitride (hBN) which has a similar lattice structure as graphene and allows a graphene electronic mobility of $3\,000\,000\text{ cm}^2/\text{Vs}$.

More importantly, this work focuses on the refinement of the transfer process of the graphene. Two different types of transfer of graphene exist, wet transfer and dry transfer. Wet transfers are using etchants and/or solvents that contribute as a source of residues in limiting the electronic mobility. On the contrary, dry transfer techniques avoid using those liquids (except solvents after transfer) and provide a significant reduction in trapped residues that considerably limit the damages on the graphene intrinsic electronic mobility.

The main goal of this master's thesis is to transfer in a dry manner chemically vapor deposited (CVD) graphene on hBN to reach the highest electronic mobility. The control of the size and the number of layers can be achieved in a cost-effective reproducible way for CVD graphene. A dry and clean delamination technique will also allow a reuse of the growth substrate.

This master's thesis report is divided in three main parts, the first one is the state-of-the-art from the literature, the second one is a presentation of the materials and methods used during the experimental work and the last one is a presentation of the results obtained.

Chapters 1 and 2 present a brief review of the literature concerning graphene and hBN, their structure, properties and different synthesis methods. Chapter 3 focuses on the different transfer techniques (dry and wet) both for exfoliated graphene and for CVD graphene. Chapter 4 goes through the different measurement techniques of the adhesion energies between graphene and other materials and summarizes different values of adhesion found in the literature to highlight the challenges of the dry transfer processes. Chapter 5 describes different measurement techniques and comparison techniques of the electronic mobility for graphene on different substrates. Chapter 6 and 7 detail the fabrication process of all the materials, the tools and the characterization methods that have been used throughout this research study. In chapter 8, the data obtained for the dry and wet transfers tested during the experimental work are presented and analyzed. Finally, this report is concluded by a summary of the main results obtained and a discussion on the future prospects.

Part I

State-of-the-art

Chapter 1

Graphene

Graphene is a two dimensional material. It is constituted of a monolayer of graphite, the most stable form of carbon under standard conditions. The group of K. Novoselov and A. Geim [1] was the first, in 2004, to demonstrate its amazing electronic properties with the production of graphene by exfoliation of Highly Oriented Pyrolytic Graphite (HOPG) and to analyze its unusual proprieties: its strength, and its ability to conduct heat and electricity. These extraordinary properties mean that it can be integrated in a huge number of applications. This chapter presents a review of the structure of the graphene and its synthesis methods.

1.1 Structure

The general structure of a graphene layer can be seen as a hexagonal lattice with one atom per vertex. This work is focused on graphene monolayer.

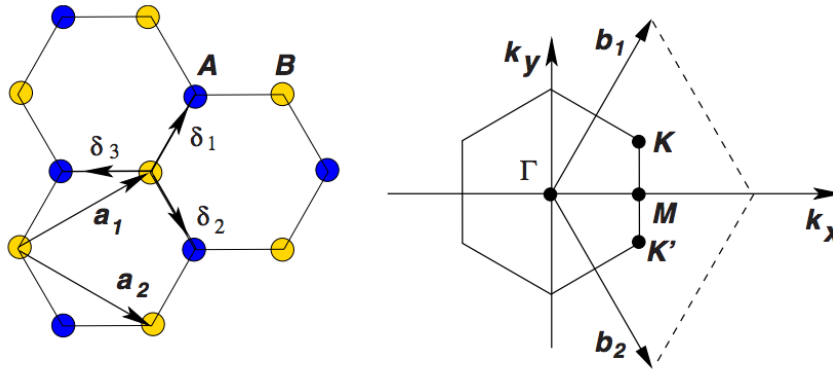


FIGURE 1.1 – Real and reciprocal lattice of graphene, hexagon in the reciprocal lattice corresponds to the Brillouin zone [2]

The lattice vector can be written as:

$$a_1 = a\left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right) \quad a_2 = a\left(\frac{\sqrt{3}}{2}, -\frac{1}{2}\right)$$

with $a = \sqrt{3}a_{cc}$ and $a_{cc} \approx 1.42 \text{ \AA}$ the carbon-carbon distance. By using the condition $a_i \cdot b_j = 2\pi\delta_{ij}$, the reciprocal lattice vectors are given by:

$$b_1 = b\left(\frac{1}{2}, \frac{\sqrt{3}}{2}\right) \quad b_2 = b\left(\frac{1}{2}, -\frac{\sqrt{3}}{2}\right)$$

with $b = \frac{4\pi}{3a_{cc}}$. This reciprocal lattice reveals the K and K' points, where the valence and conduction bands of the graphene meet up at a point called Dirac point. The energy dispersion can be described using the tight-binding approximation and is obtained as the following formula [3, 4]:

$$E_{\pm} = \pm\gamma_0 \sqrt{1 + 4\cos\frac{\sqrt{3}k_x a}{2} \cos\frac{k_y a}{2} + 4\cos^2\frac{k_y a}{2}}$$

where γ_0 represents the transfer integral between the first neighbour π orbital, k_x and k_y are the x and y components couplet with the waves vectors and E_+ and E_- are respectively associated with the valence and conduction bands. This relation is represented on the Figure 1.2.

The conduction and valence bands intersect at the zero energy level at the six corners of the Brillouin zone. Graphene is therefore considered as a zero bandgap semiconductor or a semi metal (material with a very small overlap between the bottom of the conduction band and the top of the valence band) with zero overlap. For an undoped graphene, these six corners (points K and K') are located on the Fermi level (Figure 1.2). At each of these six points, conduction and valence bands form a cone, leading to a bipolar nature for the transport of charge carriers in graphene. By changing the Fermi level, the charge carriers can either be holes or electrons. If the Fermi level increases above the Dirac point, the carriers in majority in graphene are electrons. On the other hand, if it decreases below the Dirac point, the carriers in majority are holes.

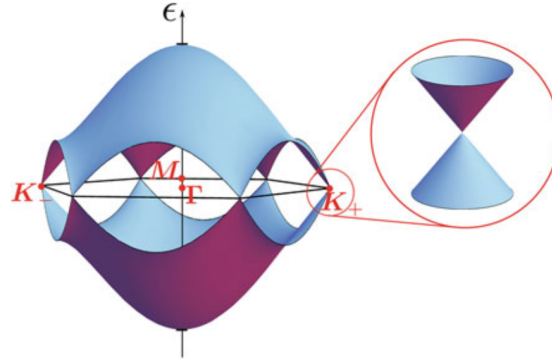


FIGURE 1.2 – Electronic band structure of graphene in the first Brillouin zone [5]

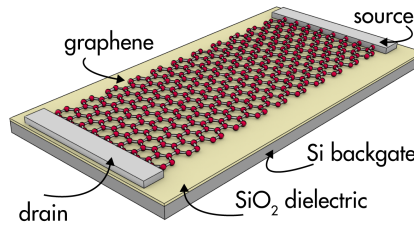


FIGURE 1.3 – Graphene monolayer in a transistor configuration [6]

If graphene is in a transistor configuration (Figure 1.3), the change of the Fermi level (and thus the modification of the type and concentration charge carriers) can be done by applying a voltage on the back-gate. Figure 1.4 shows the shape of the typical conductance function (and conductivity $\sigma = G \cdot (L/S)$, with L and S , respectively the length and the surface of the channel) of the gate voltage V_G . For a positive back-gate voltage, the Fermi level will increase and the charge carriers will be composed of electrons. For a negative voltage, the Fermi level will decrease and the charge carriers will be holes. In neutral graphene (undoped), the Fermi level

is at the Dirac point when there is no voltage applied at the back-gate. However, the presence of impurities doping graphene can shift this Fermi level and so the minimum charge carriers density will no longer be reached at 0V but at another potential called the charge neutrality point (CNP). This value allows to know the doping characteristics of the graphene sheet: if the CNP is positive, n-doped and on the contrary, if the CNP is negative, p-doped [7, 8].

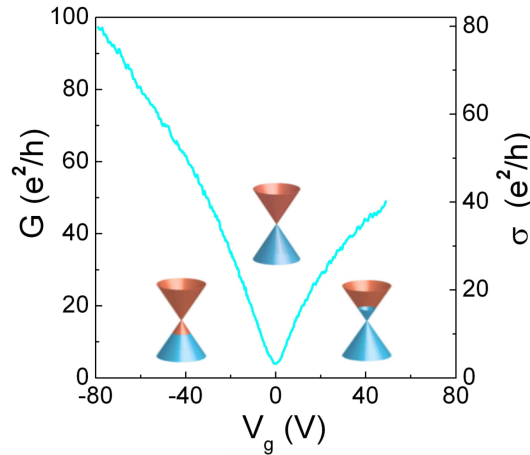


FIGURE 1.4 – Dependence of gate voltage (V_G) on the conductance (G) and on the conductivity (σ) at zero magnetic field [9]

1.2 Synthesis methods

Different methods can be used to obtain single- or few-layer graphene: mechanical and liquid phase exfoliation of graphite, chemical vapor deposition (CVD) or epitaxial growth. The goal of this section is to give a brief overview of the different ways to obtain graphene and describe these different methods.

1.2.1 Mechanical exfoliation

Mechanical exfoliation was the method used in 2004 by K. Novoselov and A. Geim [1] to produce graphene. The method consists in peeling Highly Oriented Pyrolytic Graphite (HOPG) with an adhesive tape. By the repetition of this peeling, flakes of single- or few-layer graphene can be isolated. These flakes can then be transferred on a substrate by gently pressing the tape against a silicon oxide wafer in order to deposit the graphene.

Due to its low complexity and the high quality of the flake produced, this synthesis method is very attractive. However, the size of the flakes easily varies between a few microns to one millimetre in width, and the number of flake layers is very hard to control.

To maximize the optical contrast of the carbon atom mono-layer and therefore allowing to distinguish a single from a few layer of graphene, an oxide-covered silicon wafer is used as support. The reflected light is maximal for an oxide thickness of 90 or 300 nm [10].

1.2.2 Liquid-phase exfoliation

Graphite can also be exfoliated in a liquid environment exploiting ultrasound to extract individual layer. The main steps of this process are the following: dispersion of graphite in a solvent, exfoliation, purification of single exfoliated from unexfoliated flakes (usually via ultra-centrifuging). Ideal solvents to disperse graphene are those that minimize the interfacial tension between the liquid and the graphene flakes [11].

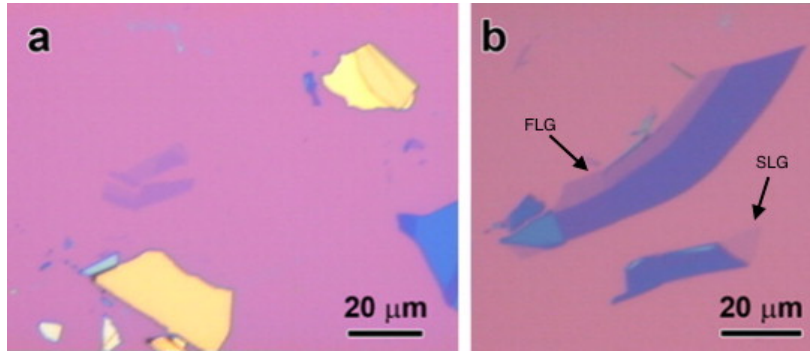


FIGURE 1.5 – Micro-mechanically exfoliated graphene. (a) thin graphite, (b) few-layer graphene (FLG) and single layer graphene (SLG) on a 300 nm SiO_2 [12]

1.2.3 Chemical Vapor Deposition

Chemical Vapor Deposition (CVD) consists in the deposition of a thin film obtained from the decomposition of one or more volatile precursors which react or decompose themselves on a metal substrate at high temperature. There are different types of chemical vapor deposition: thermal, low pressure CVD (LPCVD) or plasma enhanced CVD (PECVD). The main precursors used for the graphene synthesis are methane or ethylene. The first CVD growth of uniform large area was realized in 2009 by X. Li and C. Weiwei [13], exploiting the thermal decomposition of methane. This process was self-limited; the growth ceased as soon as the copper surface was fully covered with graphene (except around 5% of the copper area).

The current understanding of the growth chemical vapor deposition mechanism is as follows: After the decomposition from hydrocarbon, carbons atoms nucleate at the copper surface and then the nuclei grow into large domains. This nuclei density is temperature and pressure dependent. Some difficulties exist with this growth processing on most metal substrates, especially on copper because of the difference thermal expansion coefficient between copper and graphene. This thermal mismatch gives rise to a significant wrinkle density upon cooling [14].

1.2.4 Epitaxial growth

Epitaxy refers to the deposition of a crystalline overlayer, i.e. epitaxial film, on a crystalline substrate. Graphene can be obtained from the decomposition of silicon carbide (SiC) crystals at high temperature. The main advantage of thermal decomposition of SiC is that the graphene can be directly obtained on a semiconducting substrate, so no transfer is required. This method consists of annealing a commercial SiC at high temperature (between 1000 and 1700°C [15]). The vapor pressure of carbon is negligible compared to silicon. So, at high temperature, silicon atoms evaporate and leave behind carbon atoms on the surface which will then rearrange in graphitic layers [16].

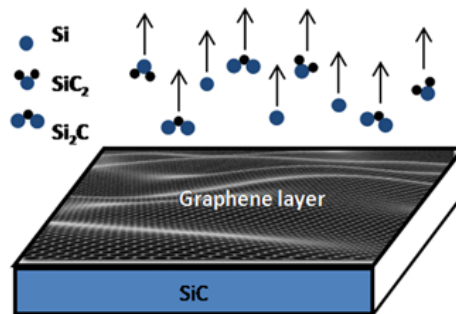


FIGURE 1.6 – Growth of epitaxial graphene on silicon carbide wafer [16]

Chapter 2

Hexagonal Boron Nitride

The hexagonal Boron Nitride (hBN), called the *white graphene*, is the preferred substrate for graphene devices, its organic analog. hBN is an industrially manufactured crystal structure of the III-V compound boron nitride. It is a heat-resistant material that is thermally stable and widely used as an electrical insulator [17, 18]. This chapter presents a review of the structure of the hBN and its synthesis methods.

2.1 Structure

A hBN monolayer has a two-dimensional honeycomb structure alternating boron and nitrogen atoms which have strong covalent bonds in the plane as seen in Figure 2.1(a). It has the same hexagonal crystal structure as the graphene, with a similar lattice constant of $a = \sqrt{3} \times a_{BN} = 2.5 \text{ \AA}$ with $a_{BN} = 1.446 \text{ \AA}$ the boron-nitrogen distance [19]. The atomic numbers in the periodic table for boron (B), carbon (C) and nitrogen (N) are respectively 7, 6 and 5. Therefore, the modelization of the electronic properties of hBN such as dispersive energy and binding energy are quite similar to the ones of the graphene.

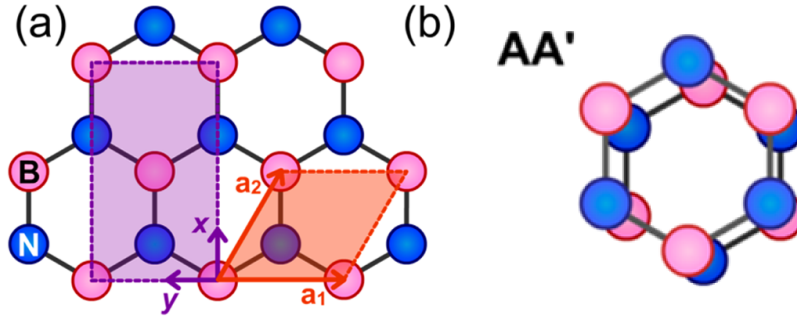


FIGURE 2.1 – Crystal structure of hBN monolayer [20]

hBN has a stable AA' stacking mode, as seen in Figure 2.1(b). The partially positively charged boron on top of the partially negatively charged nitrogen and vice versa lead to weak van der Waals forces between the different planes. The distance between two successive planes is equal to $c = 3.33 \text{ \AA}$. hBN is considered as an electrical insulator due to its direct energy gap of about 5.9 eV [21].

There is no decomposition or loss in stability at temperature as high as 1000°C in air, 1400°C in vacuum or 2850°C in an inert atmosphere [22, 23].

Its characterization can be done among others by Atomic Force Microscope (AFM), Raman or visual detection and keeping in mind that the contrast increases with the number of layers [24].

2.2 Synthesis methods

hBN can be produced by top-down methods which include exfoliating bulks of hBN crystals via mechanical or sonical methods [25, 26, 27] and bottom-up methods as Chemical Vapor Deposition (CVD) and segregation method [28].

2.2.1 Mechanical exfoliation

Layers of hBN are peeled off with adhesive tape in the same way as graphene [29, 30]. A controlled ball milling process is also able to exfoliate hBN. The rotation of a planetary mill with steel balls and hBN powder generate rolling actions of the balls which apply shearing forces on the materials [31, 32]. Perfect crystalline hBN structures can be synthesized with this method.

2.2.2 Liquid-phase exfoliation

hBN layers, from a hBN powder, are dispersed into a solvent by scattering with an intense sonication that breaks the van der Waals bonds. The sonication intensity, the time and the solvent are parameters that influence directly the number of layers and the lateral size of the flakes. Isopropyl alcohol and methane sulfonic acid can be used as solvent. Large quantities of layered hBN can be synthesized with this method.

2.2.3 Chemical Vapor Deposition

As seen in Figure 2.2, ammonia-borane or borazine are the common precursor gases used on *Ru*, *Rh*, *Rt*, *Ni*, *Pd*, *Pt*, *Ag* or *Cu* substrate [33].

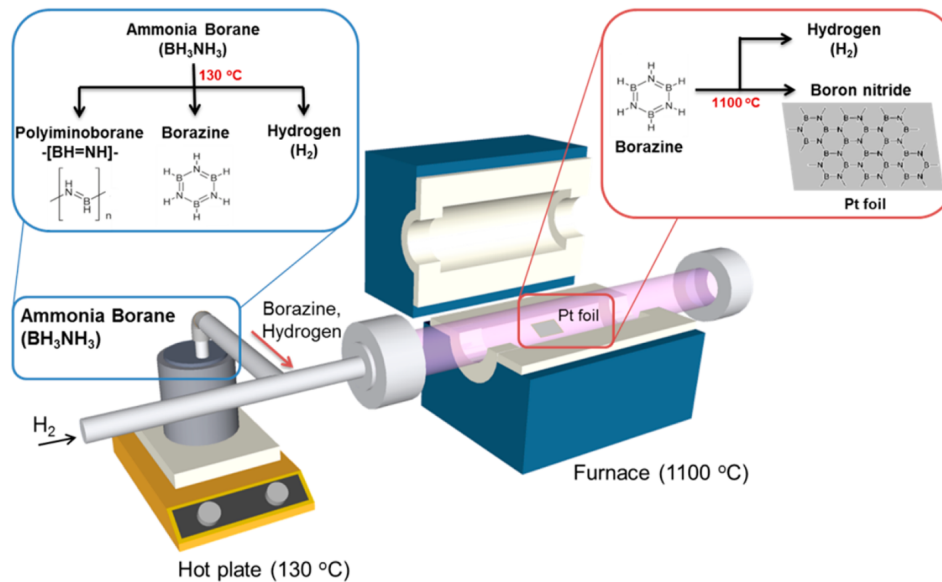


FIGURE 2.2 – LPCVD system used for hBN growth [34]

An important advantage of this method is that it permits to control the number of layers and the crystalline structure of the substance.

Chapter 3

Graphene transfer

For most of its potential applications, graphene has to be placed onto an insulator. The transfer of the graphene on this insulator could be performed either in a dry or wet manner. From previous chapter, the hBN was described as the preferred insulator for graphene.

When the graphene is obtained by CVD, the adhesion energy of the graphene with its growth substrate is very high. The most used methods to separate the graphene from its copper growth substrate are with a liquid etchant and are called wet transfer. One of the disadvantages of these methods is the amount of residues that will be trapped between the graphene and the insulator, due to the solvent or polymer used during the transfer process.

For exfoliated graphene, the best transfer methods, called dry transfers, are those that do not use solvent before the contact of the graphene and the insulator. The characteristic of such methods is that they deteriorate less the intrinsic electronic mobility of the graphene. This intrinsic property is independent on the synthesis process, CVD or exfoliation.

This chapter presents first different wet transfer techniques of CVD graphene on a target substrate then different dry transfer techniques of exfoliated graphene on hBN. It ends with a review of dry transfer technique of CVD graphene on hBN.

3.1 Wet transfer techniques

The easiest way to transfer graphene synthesized by chemical vapor deposition, and so grown on a metal substrate, is to soak the graphene/metal stack in a solution with a metal etchant. This etching can be realized using an oxidizing etchant such as $FeCl_3$ during a few minutes without forming gaseous products or precipitates. The graphene film then separates from the substrate and floats on the surface of the solution (Figure 3.1).

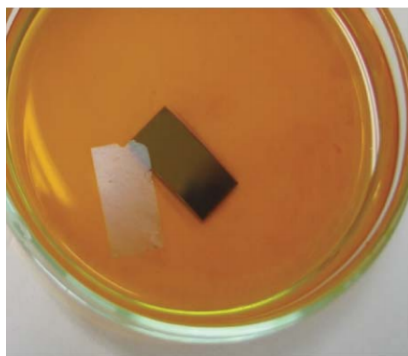


FIGURE 3.1 – Graphene film floating after etching the metal growth layer

3.1.1 Wet transfer using a PDMS supporting layer

Poly-dimethylsiloxane (PDMS) is a polymer used in graphene transfer techniques. This polymer is robust and resistant to several etchants. Moreover PDMS has a low surface adhesion force facilitating the detachment from graphene transferred to the desired substrate. The different steps constituting the transfer are the following [35]:

- A PDMS layer is applied on the graphene/metal stack.
- This structure is immersed into an etching bath to remove the metal layer. The PDMS layer will act as a support for the graphene during the etching.
- When the metal is totally etched, the structure is pulled out, rinsed and dried.
- Finally, the PDMS/graphene stack is brought in contact with the chosen substrate and since PDMS/graphene adhesion force is weaker than the one between graphene and the target substrate, the graphene is transferred and released from the PDMS.

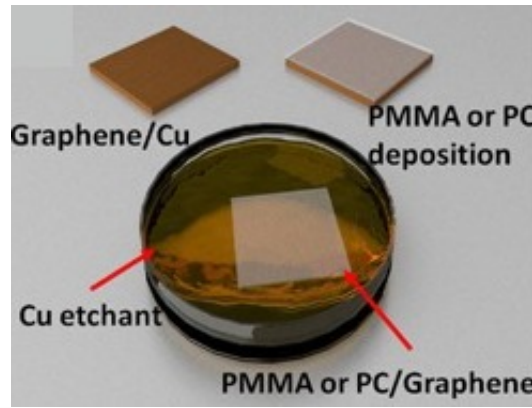
3.1.2 Wet transfer using a PMMA supporting layer

Generally, wet transfer takes advantage of a polymer as Polymethyl methacrylate (PMMA) as a supporting layer. PMMA displays many prominent features, such as the relatively low viscosity, excellent wetting capability, flexibility, and good solubility in several organic solvents [36]. The different steps of the transfer are the following [37]:

- One side of the graphene on the Cu substrate is removed with O_2 plasma in order to ensure the etch of the Cu substrate.
- A PMMA layer is coated on the graphene/copper substrate. The polymer thickness can be adjusted with the spinning rate and the PMMA concentration.
- The underlying copper substrate is etched away by an etchant (like $FeCl_3$), and the PMMA/graphene stack is rinsed in distilled water (Figure 3.2).
- The PMMA/graphene sample is fished onto the desired substrate.
- The PMMA film is dissolved by acetone, rinsed in isopropanol, and blown dry with nitrogen.

To improve the quality of the PMMA transfer, various adjustments and optimization of the classic process have been carried out. Indeed, some breaks and wrinkles occur (especially for monolayer graphene) on transferred graphene. These defects are caused by wrinkles and other defects that appeared in copper substrate during the CVD growth process. To relax the strong surface morphology and improve the contact with the substrate, an additional PMMA layer is coated onto the PMMA/graphene placed on the desired substrate after the fishing step and before the acetone step [37].

But graphene quality can also be deteriorated by PMMA residues that remain attached to the graphene after the acetone bath. Combined with the wrinkling, the residues remarkably deteriorate the structural and electrical proprieties of graphene. After the acetone bath, a thermal annealing (in a vacuum furnace at 200 to 500°C) is performed to significantly reduce these residues [38]. However, if the annealing is realized at a too high temperature, an increase in the p-type doping can take place and so potentially degrading the electrical properties of graphene.

FIGURE 3.2 – Etching of copper substrate in $FeCl_3$ [39]

3.1.3 Wet transfer using a PVA/PMMA supporting layer

This process looks like the wet transfer using only PMMA, but in this case, PMMA is not in direct contact with the graphene but in contact with Polyvinyl Alcohol (PVA) which will be dissolved in water (Figure 3.3).

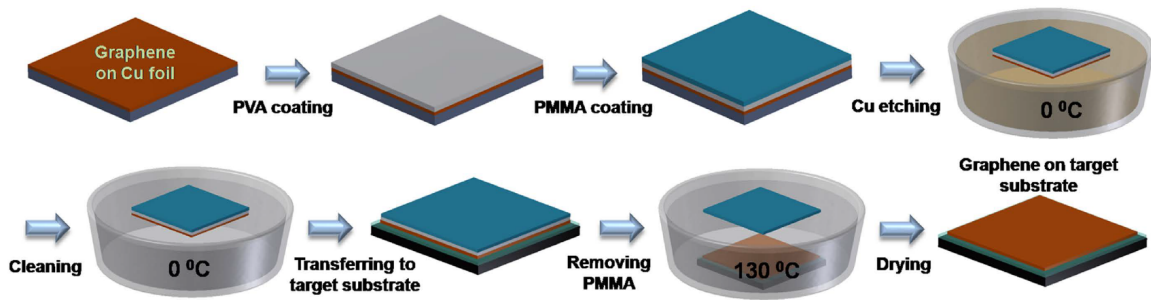


FIGURE 3.3 – PVA assisted transfer of CVD-grown two-dimensional materials [40]

This process preserves a good quality of the transferred graphene by avoiding degradation due to the PMMA etching.

3.1.4 Roll-to-roll method

As roll-to-roll method is used to transfer large scale continuous CVD graphene, this process is suitable for industrial processes. To realize this transfer, a thermal release tape (TRT) is attached to the graphene layer by two rollers. Then the copper foil is etched away using an electrochemical reaction with aqueous 0.1 M ammonium persulphate solution and the transferred graphene film on the tape is rinsed with deionized water to remove residual etchant. The graphene films are finally transferred from the polymer support onto a target substrate using a thermal treatment. A schematic overview of the process is presented in Figure 3.4 [41].

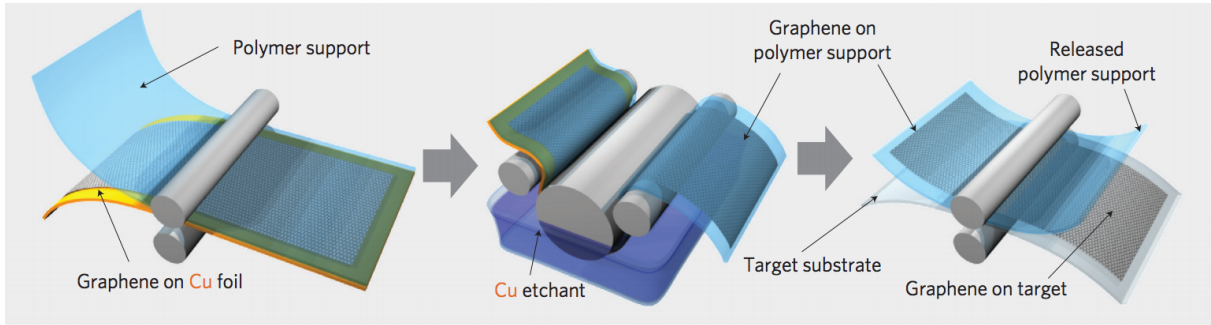


FIGURE 3.4 – Roll-to-roll graphene transfer [41]

3.1.5 Electrochemical delamination method

Another method sometimes used is the electrochemical delamination. It includes a minimal use of chemical etching to remove the growth substrate of the graphene. This method allows an industrial scalability non-destructive delamination of the graphene from the copper foil and so the reuse of the copper foil in multiple growth and delamination cycles. The different steps of the electrochemical delamination method are the following [41]:

- PMMA is spin-coated on the Gr/Cu sample. This layer will act as a protective layer.
- The stack (cathode) is immersed in an aqueous solution of $K_2S_2O_8$ (0,05 mM) (electrolyte) in which a glassy carbon (anode) is already present as seen in Figure 3.5.
- The cathode (PMMA/Gr/Cu stack) is polarized at -5V. Due to the reduction of the water: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$, hydrogen bubbles appear at the Gr/Cu interfaces.
- These bubbles provide a slight force to peel off the graphene layer from the edges of the Cu foil. Simultaneously, the presence of some etchant in the electrolyte solution induces a low dissolution of the Cu foil which is also beneficial to the graphene delamination.
- When the PMMA/Gr is completely separated from the copper, graphene is transferred onto the target substrate and the PMMA layer is removed.

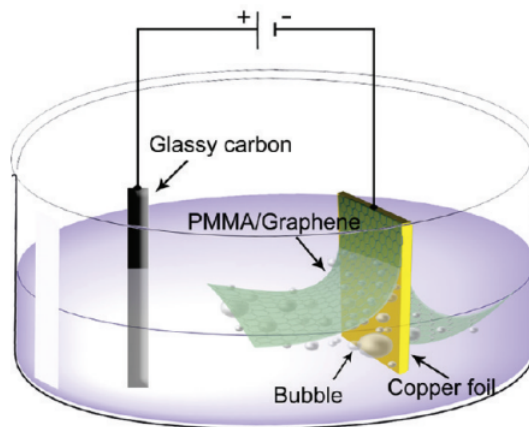


FIGURE 3.5 – Electrochemical exfoliation of graphene from Cu foil [42]

3.1.6 Wet transfer using a PDMS supporting layer without etching the copper

This method allows the reuse of the copper substrate for another CVD graphene growth process. The particularity of this method is based on the oxidation of the copper. The whole method is explained in Figure 3.6:

- A 10 nm-thick uniform fully-covered Cu_2O interlayer appears after an oxidation of the Cu/graphene performed during a few days in air with a considerable humidity level.
- A PDMS layer is set on the graphene/ Cu_2O /Cu sample, then the whole stack is immersed in a HCl solution.
- The Cu_2O is etched by the HCl and the Cu foil comes off. The PDMS/graphene stack can finally be placed onto the wanted substrate.
- The Cu foil could be re-used for a further graphene synthesis.
- The quality of the second growth is very similar to the first one as seen on the Raman spectrum. The peaks D related to the defects is absent and the ratio I_{2D}/I_G are quite the same (more information on the Raman spectrum of graphene in section 7.2.1).

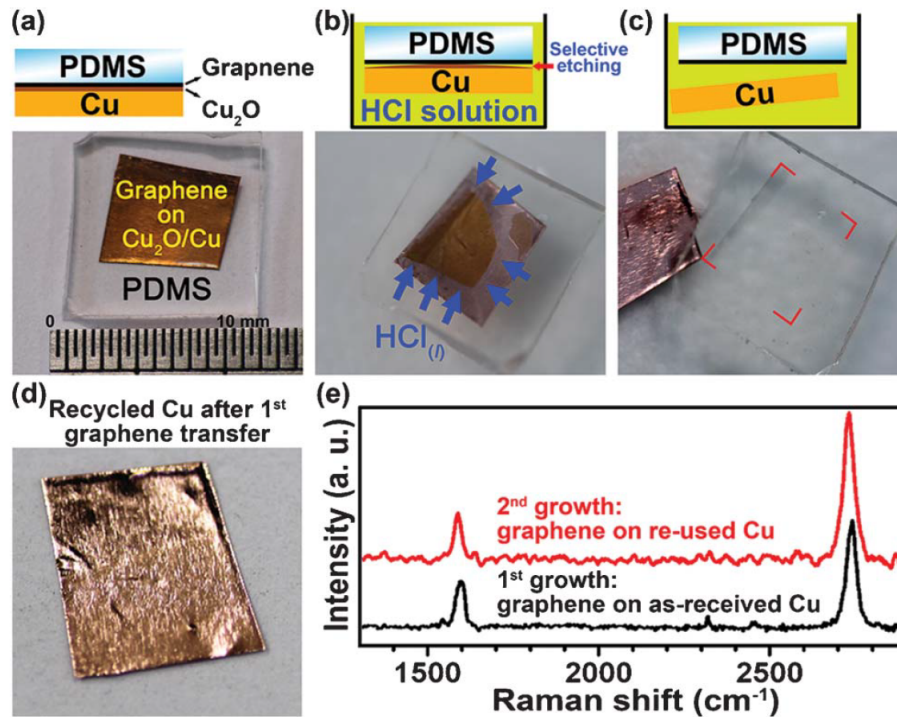


FIGURE 3.6 – PDMS assisted transfer of CVD-grown two-dimensional materials after oxidation [43]

3.2 Dry transfer techniques

To reduce the amount of residues deposited between hBN and graphene due to wet transfer, new techniques have appeared to avoid using etchants as $FeCl_3$ or HCl for copper or oxidized copper, and solvents for polymers before the transfer process. This section presents some of the most popular dry transfer techniques, for exfoliated or CVD graphene, found in the literature that will be helping in the course of this work.

3.2.1 General approach

As seen in Figure 3.7, dry transfer techniques include 3 major steps:

- **Preparation** of the
 - flake X/substrate, the acceptor substrate
 - flake Y/polymer/support, the transfer mask
- **Putting in contact** the transfer mask with the acceptor substrate. The perfectly aligned flakes in contact can be pressed together or heated and cooled down.
- **After contact**, the elements can be reassembled following three different configurations: the polymer can **be released** from the support material (Scenario A), the polymer layer can **release** a flake (Scenario B) and the polymer/flake stack can **pick-up** another flake (Scenario C).

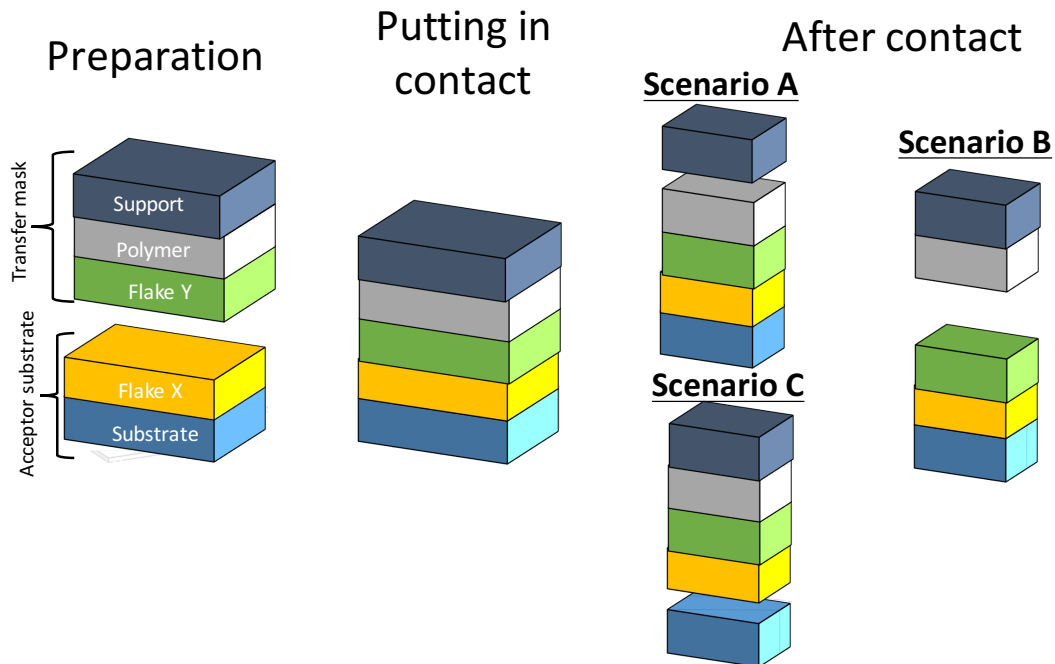


FIGURE 3.7 – Different scenarios for dry transfer technique

The different scenarios are directly influenced by the substrate, the alignment of the flakes, the polymer, the temperature (heating/cooling), the pressure (mechanical) and the disengagement rate (also called in this work separation rate, disengagement rate and displacement).

3.2.2 Exfoliated flake on polymer or on substrate

After its exfoliation (with a scotch tape, PDMS or PMMA), the flake can either be transferred on a substrate (e.g., SiO_2/Si) or either be picked up by a polymer according to its further utilization, respectively as an acceptor substrate or as a transfer mask. When using PMMA, a preheating of the transfer of the flake (100 °C) can be used to increase in average the area of the exfoliated flakes [44].

Acceptor substrate

The adhesion of the polymers is controllable with the peel-off speed thanks to their visco-elastic nature [45]. For example, with PDMS, the separation energy G_{PDMS} increases with the speed of delamination v [46, 47].

$$G_{PDMS} = G_0[1 + \phi(v, T)] \quad \text{with } \phi \text{ increasing in function of } v$$

So, to keep the flake stuck to the substrate (e.g., SiO_2/Si), a slow delamination rate is needed (see Figure 3.8). Also, to favour the flake adhesion, an oxygen-plasma treatment of the PDMS can be performed before exfoliation [48].

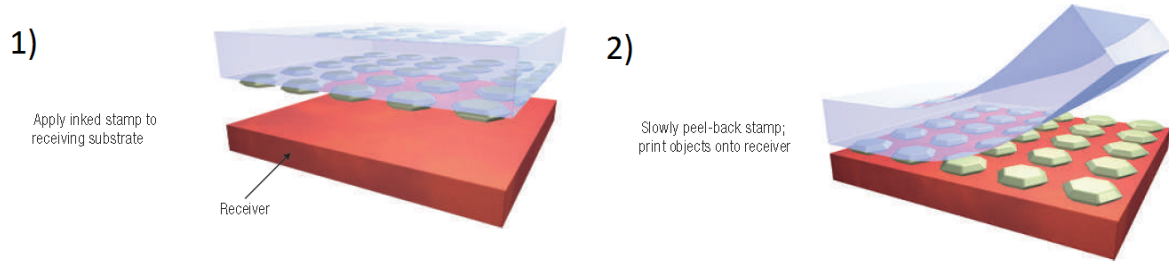


FIGURE 3.8 – Acceptor substrate [46]

Transfer mask

There are two parts in the preparation of the transfer mask. The first part is the picking up of the flake by the polymer (as seen in Figure 3.11). The other part is the method of stacking the polymer(s) on the support layer (as seen in Figure 3.12 and Figure 3.13).

The picking up of the flake can be done immediately by getting in contact the scotch tape with the target flake and the polymer (Figure 3.9).

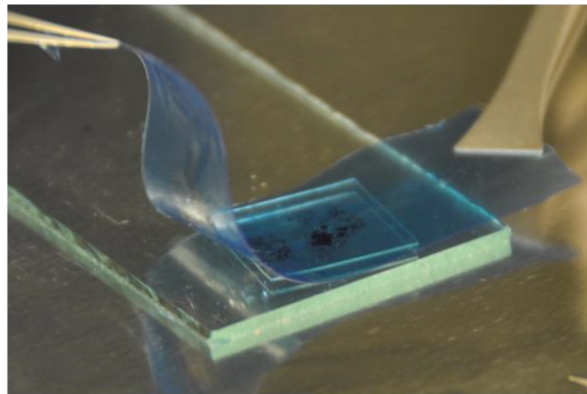


FIGURE 3.9 – Picking up of the flake of graphene by the polymer [45]

Wang et al. picked up the hBN flake from the scotch tape for the transfer mask with a polypropylene carbonate (PPC)/PDMS stack of polymers [49].

Joel et al. picked up the hBN flake for the transfer mask with a PMMA/PDMS stack of polymers heated up to 110°C then cooled down to 90 °C before a quick disengagement. They also picked up another hBN flake for a transfer mask with a PPC/tape/PDMS stack of polymers heated up to 30°C during 3 min then they disengaged quickly [50].

Uwanno et al. picked up the hBN flake for the transfer mask with a PMMA/PDMS stack of polymers at 90°C [45].

Zimmerman et al. picked up the hBN flake for the transfer mask with a PPC/PDMS stack of polymers by heating up to 40°C then cooling down before disengagement [51].

The picking up of the flake can be done using an intermediate material. The target flake on the scotch tape is transferred onto the intermediate material and then the target flake is picked up by the polymer from the intermediate material. The flake can be picked up by heating during contact (Figure 3.10) or by choosing the right disengagement rate (Figure 3.11).

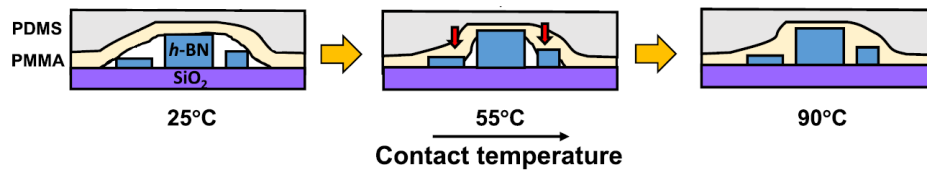


FIGURE 3.10 – Picking up of a flake of hBN on an intermediate material (SiO_2) by a stacking of polymers (PMMA/PDMS) [45]

Wang et al. picked up the hBN flake from SiO_2 , the intermediate material, for the transfer mask with a PPC/PDMS stack of polymers and heated up to 40°C during contact [49].

Uwanno et al. picked up the hBN flake from SiO_2 , the intermediate material, for the transfer mask with PMMA/PDMS stack of polymers and heated up to 90°C during contact [45].

Meitl et al. used PDMS and a quick delamination rate to grab objects [46].

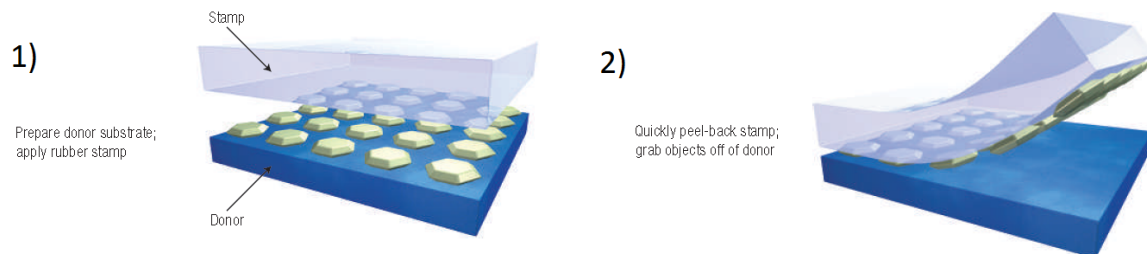


FIGURE 3.11 – Picking up of a flake on an intermediate material (donnor) by a polymer (PDMS) [46]

The two main methods used for the stacking of polymer(s) on the support layer for the fabrication of the transfer mask are: the "water-soluble layer (WSL) transfer" method and the "low glass transition temperature (T_g) polymer" method [45].

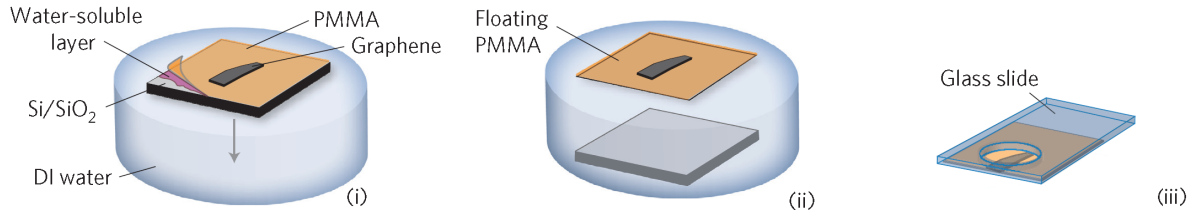


FIGURE 3.12 – Stacking polymer(s) on the support layer by the "WSL transfer" method [52]

As seen in Figure 3.12 for the "WSL transfer" method, the preparation of the transfer mask starts with graphene/polymer/water-soluble layer/*Si* wafer. (i) The stack is deposited on a deionized water bath while trying to avoid contact between the graphene and the water. (ii) Once the water-soluble layer has dissolved, the support layer sinks to the bottom of the bath while the polymer/flake is floating. (iii) The stack is scooped, dried then adhered to a glass transfer slide (or a metal ring [44]).

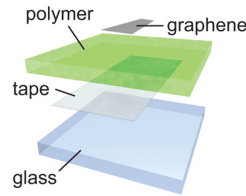


FIGURE 3.13 – Stacking polymer(s) on the support layer by the "low T_g polymer" method [53]

As seen in Figure 3.13 for the "low T_g polymer" method, after exfoliation the flakes are immediately transferred onto a glass slide/polymer(s) stack. The polymer in contact of the flake is a low T_g polymer (a polymer becomes soft at a temperature higher than its T_g).

3.2.3 Exfoliated graphene on exfoliated hBN

All the methods described in this section put into contact exfoliated flakes that are on the two following stacks:

- **graphene**/polymer/support, the transfer mask
- **hBN**/substrate, the acceptor substrate

Those processes have only **one** contact of the flakes.

Scenario A & Scenario B & Scenario C (Figure 3.7)

- Before the contact, the graphene flake is on a polymer layer on a supporting glass slide (with or without another low T_g). They will be called graphene/first polymer/second polymer/glass. The hBN flake is placed on *SiO₂/Si*. The glass slide with the polymer(s) and the graphene flake is placed onto a micromanipulator above the hBN flake. The graphene needs to be perfectly aligned with the hBN before putting them in contact.

- Then, with the use of a micromanipulator, the two flakes are brought into contact and heated.
- Scenario A: The temperature increase softens the polymer(s) and the first polymer will stay on the SiO_2 after the disengagement. A solvent will be used to remove the polymer of the stack of $Si/SiO_2/hBN/graphene/polymer$. The last step is a thermal annealing in Ar/H_2 during a few hours at high temperature to remove resistant residues.

Scenario B: The temperature increase softens the polymer(s) and the graphene flake is released by the PMMA carrier film and deposited on top of the second crystal of SiO_2 . No solvent will be used only a thermal annealing to remove resist residues.

Scenario C: The temperature increase softens the polymer(s) and the graphene flake is picked up by the hBN/PMMA carrier film.

Scenario A

The **first** group of methods includes the methods in which use the polymer from the graphene/polymer/support stack as a sacrificial layer. **The support releases the graphene/polymer after contact** (Scenario A). The polymer needs to be dissolved afterwards.

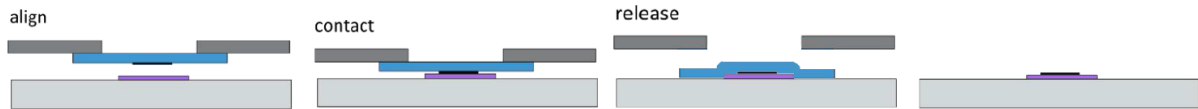


FIGURE 3.14 – Scenario A, modified from [44]

Dean et al. used the "WSL transfer" method with graphene/PMMA/PVA/Si wafer as intermediate stack for the transfer mask and graphene/PMMA/glass slide as transfer mask. At contact, the acceptor substrate is heated up to 110°C . After transfer, acetone is used to dissolve PMMA followed by a thermal annealing in Ar/H_2 during 3.5 hours at 340°C [52].

Zomer et al. used the "low T_g polymer" method with graphene/evalcote/adhesive tape/glass as transfer mask. At contact, a temperature between $75\text{--}100^\circ\text{C}$ is needed to allow the adhesive tape to release the low glass temperature polymer that melts. After transfer, acetone/IPA is used to dissolve evalcote followed by a thermal annealing in Ar/H_2 during 8 hours at 330°C [53].

Leon et al. annealed the acceptor substrate before contact (500°C during 2 to 3h in a Ar/O_2 flow). They used the "WSL transfer" method with PVA as water-soluble layer and an aluminum slide with a hole for the support layer of the transfer mask. At contact, the temperature is increased up to 110°C during 10 minutes. After transfer, acetone/IPA is used to dissolve PMMA followed by a thermal annealing in Ar/H_2 during 3 hours at 400°C [54].

Uwanno et al. used the "low T_g polymer" for the transfer mask by spin-coating a $1\text{ }\mu\text{m}$ -thick layer of PMMA on polydimethylsiloxane (PDMS)/glass slide. The acceptor substrate is a hBN flake exfoliated onto n^+-Si/SiO_2 . The transfer is heated up 55°C more than 5 min [45].

Zimmerman et al. used the "WSL transfer" method with graphene/PMMA/PVA/ SiO_2/Si^{++} as intermediate stack for the transfer mask and graphene/PMMA/glass slide for the transfer mask. At contact, the temperature is increased up to 120°C during 15 minutes. After transfer,

acetone is used to dissolve PMMA followed by a thermal annealing in H_2 (it was the only possibility in their facilities) during 0.5 hour at 350 °C [51].

Scenario B

The **second** group of methods includes the methods in which **the polymer from the graphene/polymer/support stack releases the graphene after contact** (Scenario B). It is called the all-dry release transfer process because no solvent will be used.

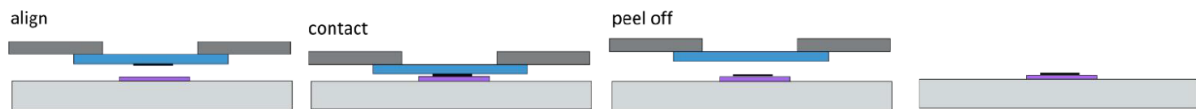


FIGURE 3.15 – Scenario B [44]

Kretinin et al. used the "WSL transfer" method for its transfer mask with polymethylglutarimide (PMGI) for the water-soluble layer. The floating PMMA/graphene stack is picked up on a metal ring. During contact, the PMMA will release the flake with an optimal temperature of 60-70°C only if it has strong adhesion to the substrate. After disengagement, a thermal annealing is performed in Ar/H_2 by those following steps: for 0.5 hour at 100°C, for 0.5 hour at 200°C and for 3 hour at 300°C [44].

Castellanos et al. stacked graphene for the transfer mask directly on PDMS/glass slide. Heat is not needed during contact but rather a **pressure** on the stamp against the acceptor substrate. For the disengagement the stamp is peeled off very slowly [55].

Uwanno et al. used the "low T_g polymer" method. They decided for the stacking of the PMMA/PDMS/glass slide to spin-coat on the PDMS the PMMA with a thickness of 1 μm . The hBN flake is exfoliated onto n^+-Si/SiO_2 . A Peltier module is used for the heating system during the contact. The temperature rises up to 55°C during less than 3 minutes. Then, the whole stack needs to be **cooled down** before disengagement. The **displacement rate** has to be less than 80 $\mu m/s$. After transfer, a thermal annealing is performed in Ar/H_2 during 3 hours at 200°C [45].

Tien et al. used a combination of the "WSL transfer" method and the "low T_g polymer" method. They started by doing a stacking of graphene/PMMA/PVA/Si. They placed the stack in a water bath while trying to avoid contact between the graphene and the water. The floating PMMA was then adhered to a transparent PDMS stamp attached to a glass slide. An isotropic pressure is applied on the target substrate to improve the success rate of the transfer [56].

Scenario C

The **third** group of methods includes the methods in which **the hBN from the hBN/polymer/support stack picks up the graphene after the first contact** (Scenario C).

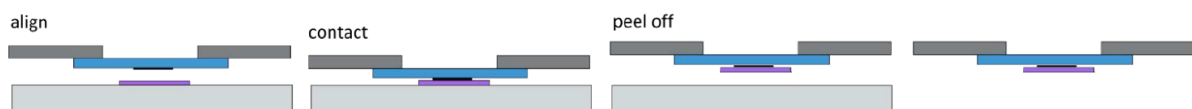


FIGURE 3.16 – Scenario C, modified from [44]

Uwanno et al. used the "low T_g polymer" method. They opted for the stacking of the PMMA/PDMS/glass slide to spin-coat on the PDMS the PMMA with a thickness of 1 μm . The hBN flake is exfoliated onto $\text{n}^+\text{-Si/SiO}_2$. A Peltier module is used for the heating system during the contact. More than 3 min but less than 5 min and the hBN is peeled off during disengagement. Then, the whole stack needs to be **cooled down** before disengagement. The **displacement rate** needs to be bigger than 80 $\mu\text{m/s}$ to guarantee that the hBN flake will be picked-up [45].

3.2.4 Exfoliated graphene encapsulated in exfoliated hBN

In the case of encapsulated graphene in hBN, the carbon sheet is in contact with the top and bottom hBN flakes. Four situations are possible for this process with a succession of two different scenarios for the **two** contacts of the flake of graphene with one flake of hBN first and then with another flake of hBN:

Situation	First contact	Second contact
1	Upper flake released (Scenario B)	Polymer released (Scenario A)
2	Upper flake released (Scenario B)	Upper flake released (Scenario B)
3	Lower flake picked-up (Scenario C)	Polymer released (Scenario A)
4	Lower flake picked-up (Scenario C)	Upper flake(s) released (Scenario B)

TABLE 3.1 – The four different ways to encapsulate graphene into two exfoliated hBN

At the first contact, there are two possibilities of methods that are used: the pick-up technique and the release technique. The release technique is the release of the flake from the polymer. The pick-up technique is the pickup of one flake by the other one.

At the second contact, there are also two possibilities of methods that are used: the release technique and the "be released" technique. The "be released" technique is the release of the polymer from the support layer.

If at the first contact, it is a "be released" technique, it will be no longer considered as a dry transfer [57] (because of the use of a solvent before the end of the final stack).

Situation 1: Scenario B followed by Scenario A

Situation 1 is a bottom to top technique. **The polymer from the graphene/polymer/-support stack releases the graphene after the first contact (Scenario B). The support releases the hBN/polymer after the second contact (Scenario A).**

Kretinin et al. continued the stacking of flakes with a "be released" technique for the second contact. The last step is the removing of the polymer with acetone followed by a thermal annealing (100°C for 30 min, 200°C for 30 min and 300°C for 3 hours) [44].

Situation 2: Scenario B followed by Scenario B

Situation 2 is a bottom to top technique. **The polymer from the graphene/polymer/-support stack releases the graphene after the first contact (Scenario B). The polymer from the hBN/polymer/support stack releases the hBN after the second contact (Scenario B).**

Tien et al. continued the stacking of flakes with a release technique for the second contact. The temperature is increased up to 90°C during 10 min while applying an isotropic pressure as for the first contact [56].

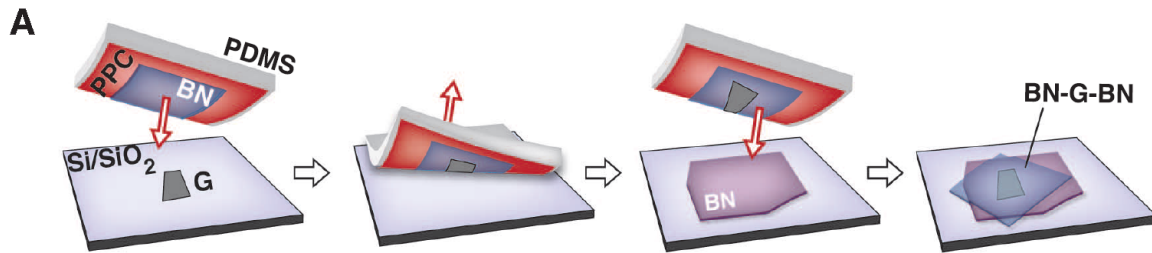


FIGURE 3.17 – Pick-up/release technique for encapsulated exfoliated graphene into exfoliated hBN [49]

Situation 3: Scenario C followed by Scenario A

Situation 3 is a top to bottom technique (see Figure 3.17). **The hBN from the hBN/polymer/support stack picks up the graphene after the first contact (Scenario C). The support releases the hBN/polymer after the second contact (Scenario A).**

Wang et al. used an exfoliated hBN on PPC/Si for the pick-up technique. Then, the PPC is manually peeled off from Si and placed on PDMS on a glass slide. At the first contact, the PPC/hBN will pick up the flake of graphene with a temperature stage of 40°C for the best results. The whole stacking is then brought into contact with a second flake of hBN previously exfoliated on SiO_2 . At the second contact, the PPC will soften with a temperature of 90°C. After contact, PPC is removed with chloroform [49].

Joel et al. exfoliated hBN on SiO_2/Si with PMMA. A thermal annealing is performed in Ar/H_2 during 3 hours at 350°C. Then, the flake is picked-up by PMMA (or PPC) that is spin-coated on top of tape/PDMS/glass slide at 100°C for the PMMA (or 30°C for PPC). A quick movement is used for the disengagement. For the release process, after contact the temperature is increased until 140 - 150°C for PMMA (or 70 - 80°C for PPC) and, after cooling, the disengagement is as slow as possible. To remove the polymer, acetone or chloroform is used during 5 min and a thermal annealing is performed in Ar/H_2 atmosphere at 350°C for 3 hours [50].

Situation 4: Scenario C followed by Scenario B

Situation 4 is a top to bottom technique. **The hBN from the hBN/polymer/support stack picks up the graphene after the first contact (Scenario C). The polymer from the hBN/polymer/support stack releases the hBN after the second contact (Scenario B).**

Zimmerman et al. began with a stacking of PPC/PDMS/glass side. Each flake is picked up after contact (40°C then cooled before disengagement). There are two options for the last contact because the temperature used is more than 40°C. Either the polymer is released from its support, or the flake is released from the polymer [51].

3.2.5 Exfoliated: Summary

References	Contact [$^{\circ}\text{C}/\text{min}$]	first polymer	second polymer	displacement rate
Joel, 2015 [50]	100 $\rightarrow$ 90 30/3	PMMA PPC	PDMS tape/PDMS	quick quick
Uwanno, 2015 [45]	90	PMMA	PDMS	
Zimmerman, 2016 [51]	40**	PPC	PDMS	

TABLE 3.2 – Exfoliated flake picked up by a polymer stack **if cooling before disengagement

References	Contact [$^{\circ}\text{C}/\text{min}$]	Annealing [$^{\circ}\text{C}/\text{hour}$]	first polymer	second polymer	Solvent
Dean, 2010 [52]	110	340/3.5	PMMA	-	acetone
Zomer, 2011 [53]	75-100	330/8	evalcite	adhesive tape	acetone/IPA
Wang, 2013 [49]	90	-	PPC	PDMS	chloroform
Leon, 2014 [54]	110/10	400/3	PMMA	-	acetone/IPA
Joel, 2015 [50]	140 70-80**		PMMA PPC	tape/PDMS tape/PDMS	chloroform acetone
Uwanno, 2015 [45]	55/>5		PMMA	PDMS	
Zimmerman, 2016 [51]	120/15 >40	350/0.5	PMMA PPC	- PDMS	acetone

TABLE 3.3 – First group of methods for transfer of exfoliated graphene with the use of solvent for the polymer after contact (Scenario A) **if cooling before disengagement

References	Contact [°C/min]	Annealing [°C/hour]	First polymer	Second polymer	Displacement rate [$\mu\text{m/s}$]	pressure
Kretinin, 2014 [44]	60-70	300/3*	PMMA	-	-	-
Castellanos, 2014 [55]	room	-	PDMS	-	slow	yes
Uwanno, 2015 [45]	55/<3**	200/3	PMMA	PDMS	<80	
Tien, 2016 [56]	90/10	-	PMMA	PDMS		yes
Zimmerman, 2016 [51]	>40		PPC	PDMS		

TABLE 3.4 – Second group of methods for transfer of exfoliated graphene without the use of solvent for the polymer after the first contact (Scenario B) **if cooled before disengagement *other steps for the annealing

References	Contact [°C/min]	First polymer	Second polymer	Displacement rate
Wang, 2013 [49]	40	PPC	PDMS	
Joel, 2015 [50]	100 30/3	PMMA PC	tape/PDMS tape/PDMS	quick quick
Uwanno, 2015 [45]	55/3-5 55/<3	PMMA PMMA	PDMS PDMS	>80 $\mu\text{m/s}$
Zimmerman, 2016 [51]	40**	PPC	PDMS	

TABLE 3.5 – Third group of methods for the pick up of the exfoliated graphene by the hBN/polymer stack (Scenario C) **if cooled before disengagement

From those different scenarios, some conclusion can be drawn:

For a same transfer mask, the temperature/time and the disengagement rate will have a huge impact on the final state after contact.

For a same stack of polymers, at high temperature (140°C for PMMA/PDMS, more than 40°C for PPC/PDMS): the polymer(s) will be released from the support, and at lower temperature (100°C for PMMA/PDMS, 40°C for PPC/PDMS): the polymer will pick up the flake.

For a same stack, at a certain temperature (50°C for PMMA/PDMS), the three scenario could happen in function of the duration of contact of the flakes. From longest to the shortest duration of contact: release of the polymer from the support, pick up of the lower flake, and release of the upper flake. The temperature at contact for the picking up of a flake is the same for a polymer or a transfer mask of flake/polymer.

3.2.6 Graphene CVD on polymer

In this section, the different techniques found in the literature to delaminate graphene from copper with a polymer will be presented. The flake picked up on the polymer will be further transferred on hBN.

Lock et al. enhanced the adhesion between the polymer layer and the graphene by modifying surface chemistry with azide as seen in Figure 3.18. The graphene is delaminated with an adhesion-treated polystyrene (PS). PS is firstly treated during one minute in carbon dioxide plasma introducing oxygen functional groups as hydroxyls, carboxyls, and carbonyls. The surface chemistry of polystyrene is modified to enhance adhesion after plasma treatment with an azide linker molecule dip coated for two hours on the polymer. Azides provide strong heat activated covalent bonds to graphene. Using a Nano Imprinter machine at a pressure of 500 psi (= 34 bar) for 30 min at a temperature of 150°C allows the formation of covalent carbene bond between graphene and polymer. The last step is the separation of the polymer/azide/graphene stack from the Cu foil [58].

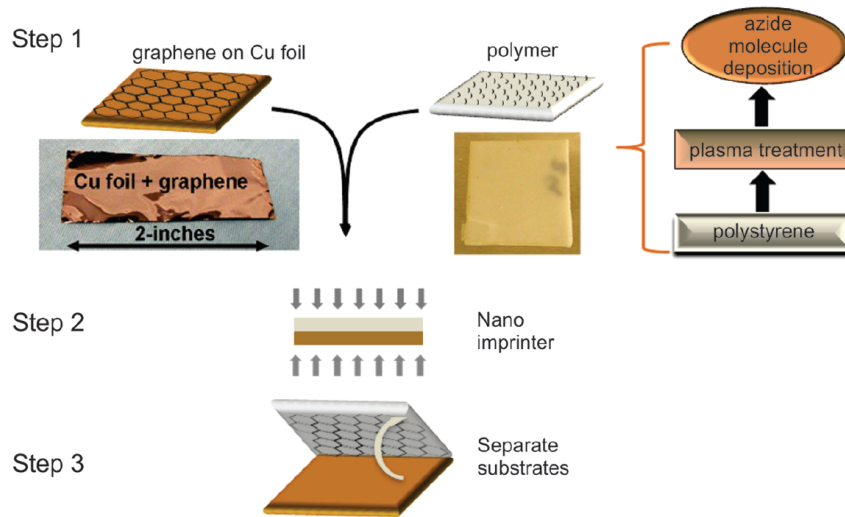


FIGURE 3.18 – Delamination of graphene by adhesion-treated polystyrene [58]

Yoon et al. delaminated graphene from *Cu* substrate with epoxy by using a specific rate for the separation (Figure 3.19). If the substrate is a foil of copper, the delamination rate needs to be higher than $5 \mu\text{m/s}$. If the substrate is a thin film of copper, the delamination rate needs to be less than $42 \mu\text{m/s}$ [59].

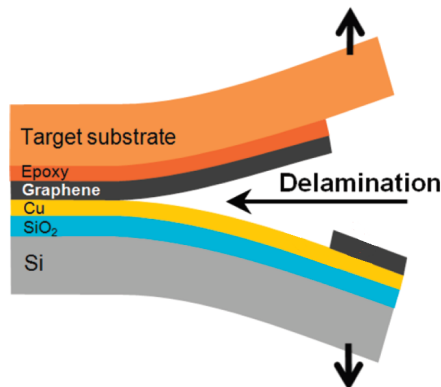


FIGURE 3.19 – Delamination of graphene with epoxy [59]

In Figure 3.20, Jung et al. enhanced the adhesion between the polymer layer and the graphene with temperature, physical pressure and voltage under vacuum (10mTorr). A PDMS layer is placed on graphene on copper foil between two electrodes. After the MET process, the *Cu* foil is separated from the graphene on PDMS with tweezers. Some values for the temperature and the applied voltage can be found in the Figure 3.21 (also for glass and PET).

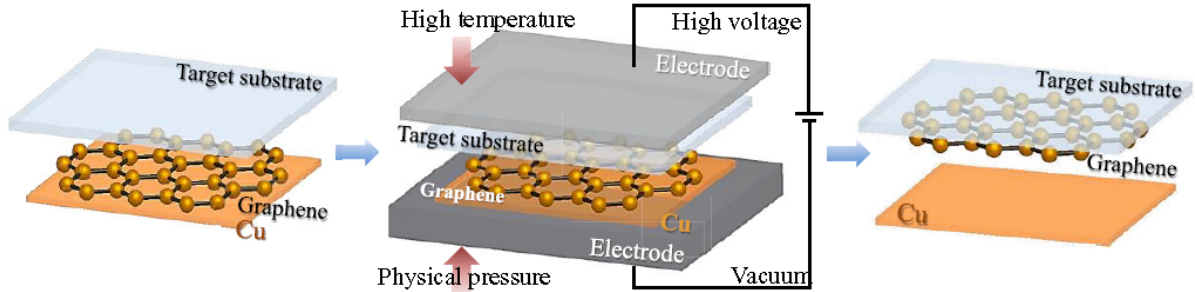


FIGURE 3.20 – Delamination of graphene by a mechano-electro-thermal (MET) process [60]

Some values for the temperature and the applied voltage can be found in the Figure 3.21 (also for glass and PET).

Target substrate	PET	PDMS	Glass
Completely exfoliated	185 ~ 200 (°C) and 600 ~ 900 (V)	~ 185 (°C) and ≥ 900 (V)	≥ 160 (°C) and ≥ 900 (V) ≥ 420 (°C) and ≥ 200 (V)
Partially exfoliated	140 ~ 170 (°C) and 600 ~ 900 (V) 170 ~ 200 (°C) and 300 ~ 600 (V)	130 ~ 160 (°C) and ≥ 900 (V)	260 ~ 360 (°C) and ≤ 600 (V)
Not exfoliated	≤ 140 (°C) 140 ~ 170 (°C) and ≤ 300 (V)	≤ 130 (°C) and 0 (V)	≤ 260 (°C) and 0 (V)
Hazed/Thermal deflection	≥ 185 (°C) or ≤ 110 (°C)	≥ 180 (°C)	420 (°C)

FIGURE 3.21 – Delamination of graphene by a mechano-electro-thermal (MET) process [60]

In Figure 3.22, Fechine et al. enhanced the adhesion between the polymer layer and the graphene with temperature and pressure. A polymer substrate is placed atop graphene on copper foil between the two plates of an Hot Press Machine (HPM). This equipment is supplied with a heating/cooling system and a pressure controller. The stack is heated up to $T = 10...20$ + the melting temperature of the polymer during 5 min with a moderate pressure of 350kPa then cooled down. A polymer/graphene/copper stack is removed from the HPM and the copper substrate is peeled out leaving a polymer/graphene stack.

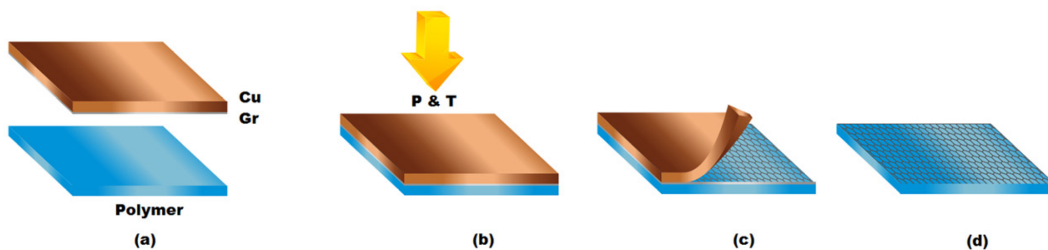


FIGURE 3.22 – Delamination of graphene by temperature and pressure control [61]

Luo et al. minimized the adhesion between graphene and the copper substrate with oxidation and enhanced the adhesion between polymer and graphene with temperature as seen in Figure 3.23. The metal foil with graphene is placed on a plastic Petri dish that floats on deionized water in a Teflon container. The container is sealed then heated up to expose the graphene/copper to water-saturated-air. The optimal temperature and time value found is 50 °C during 48h. A poly(bisphenol A carbonate) (PC) layer ($\simeq 50\mu\text{m}$) is then spin-coated on top of the pretreated stack. To increase the adhesion between graphene and polymer, an annealing is performed at 150 °C during 10 minutes. When the stack has cooled to room temperature, the PC/graphene stack is peeled off from the metal foil with tweezers. After contact of the flake on the target substrate, high voltage is applied to ensure electrostatic bonding. Another layer of PC is spin-coated on the first one then the stack is annealed at 100 °C for 10 minutes. Chloroform is used to remove the PC layer.

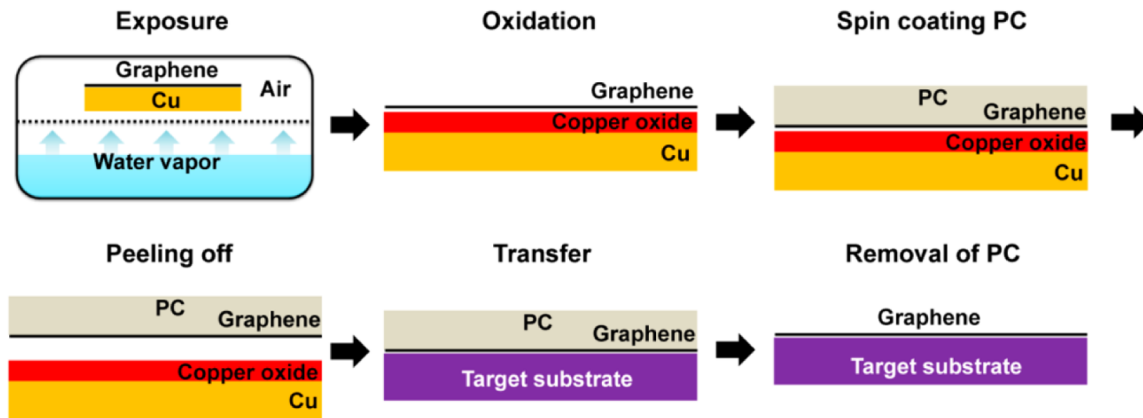


FIGURE 3.23 – Delamination of graphene after water oxidation of copper [62]

As seen in Figure 3.24, the reuse of the copper is possible for several graphene growths while keeping good structural integrity [62].

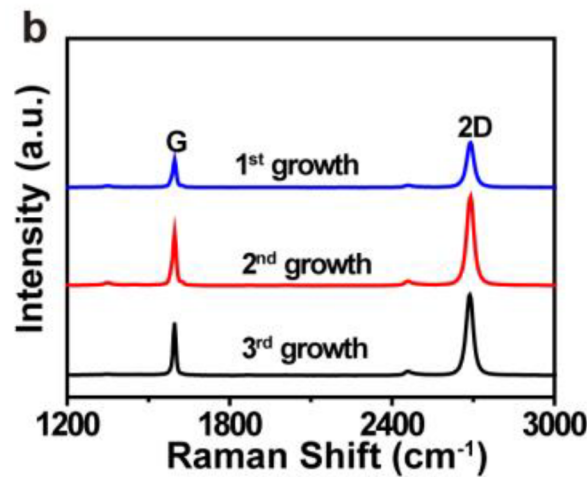


FIGURE 3.24 – Raman of graphene on reused copper [62]

3.2.7 Graphene CVD on exfoliated hBN

In 2013, Yang et al. proposed to exfoliate hBN on Si/SiO_2 and then to grow graphene on top of it by chemical vapor deposition. To remove tape residues of the exfoliation, a thermal annealing

is performed in H_2 for 30 min just after the exfoliation of hBN. Then graphene grows under remote plasma-enhanced CVD (R-PECVD) at 500 °C with methane as the carbon source [63].

3.2.8 Graphene CVD on hBN CVD

Kim et al. proposed in 2013 to grow firstly hBN on copper by chemical vapor deposition and then to grow graphene on top of it also by chemical vapor deposition (Figure 3.25). The hBN grows under low pressure chemical vapor deposition (LPCVD) at 1000 °C with ammonia borane as precursor. Then, at the same time, the hBN precursor is turned off and the graphene precursor is introduced. Methane is used, while the temperature remains the same. The graphene growth time is limited to 10 - 20 seconds [64].

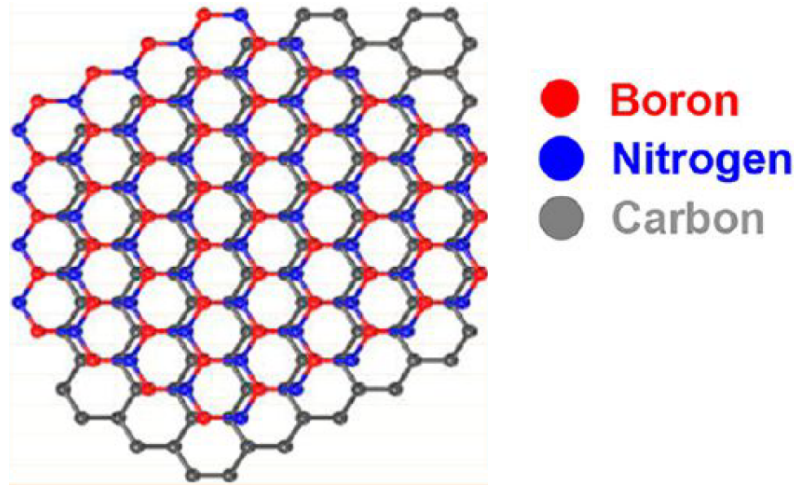


FIGURE 3.25 – AA-stacking of hybrid structure of graphene on hBN [64]

3.2.9 Graphene CVD encapsulated into two exfoliated hBN

Situation 3 and 4 are applicable with graphene synthesized by CVD. Here, two examples found in the literature.

Banszerus et al. encapsulated CVD graphene into two exfoliated hBN (Figure 3.26) [65].

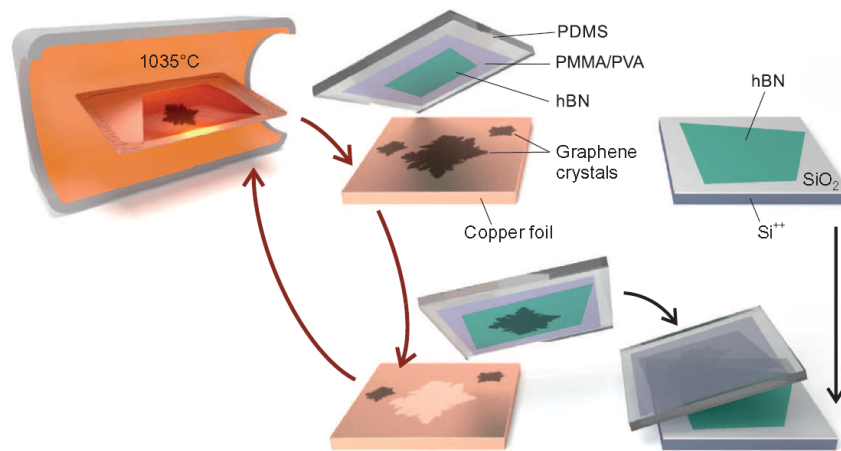


FIGURE 3.26 – Dry transfer CVD graphene encapsulated into two hBN [65]

Before the first contact, the "low T_g polymer" method is used for the transfer mask. Exfoliated hBN is placed onto PMMA/PVA/glass slide. hBN/PMMA/PVA is then placed on PDMS/glass

slide. The hBN flake is brought into contact with a graphene flake on its copper substrate. The temperature during the contact is increased to 125°C. After lifting the stack, the flake of graphene is picked up by the other hBN flake (Scenario B). On one hand, the stack of flakes is brought into contact with another hBN flake on SiO_2/Si and, after this second contact, the polymer is removed in water and acetone (Scenario A). On the other hand, the copper can be reused as a substrate for graphene growth by CVD (Figure 3.27).

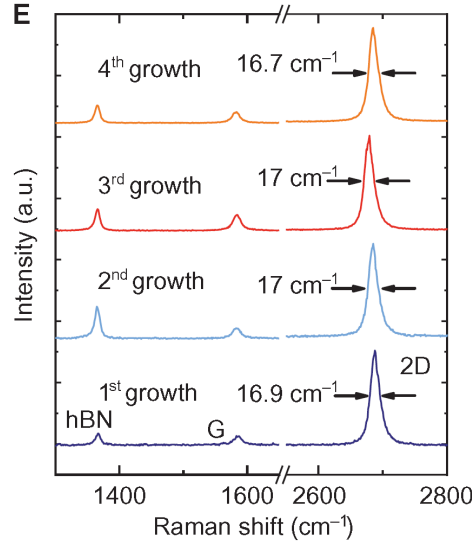


FIGURE 3.27 – Raman of graphene on hBN from reused copper [65]

Schmitz et al. delaminated bilayer graphene (BLG) from its oxidized copper substrate. Oxidation is performed during minimum 5 days in ambient air. The transfer mask is a hBN/PMMA/PVA/PDMS stack. At the flakes contact, the temperature is heated up to 125 °C during one minute. After the pick-up of the BLG, the flakes are put into contact with another flake of hBN exfoliated on SiO_2/Si [66].

Chapter 4

Adhesion energy

Graphene and hBN are considered as two-dimensional materials. It means that their surface to volume ratio is very high. In such case, the surface forces shall be taken into account for the determination of the adhesion energy. The interaction forces are dependent on the van der Waals forces, the capillary effects and the surface roughness. Other surface conditions like moisture, chemical reactivity, etc. can also contribute. This chapter presents a review of measurement techniques and simulation methods to calculate the adhesion energy between graphene and substrates as hBN, copper, SiO_2 . It ends with some measurement values.

4.1 Basic principles

First, here are the four main basic principles to keep in mind when further reading this chapter.

- The adhesion energy $\Gamma_{adhesion}$ between two dissimilar materials is determined as follows:

$$\Gamma_{adhesion} = \gamma_1 + \gamma_2 - \gamma_{12} [J/m^2]$$

with γ_1 the surface energy of material 1, γ_2 the surface energy of material 2 and γ_{12} the surface energy of the interface between material 1 and 2.

- The Hooke's law defines the relation between the stress and the deformation:

$$\sigma = E\epsilon \quad \text{with} \quad \sigma = \frac{F}{S} [Pa] \quad \text{and} \quad \epsilon = \frac{l - l_0}{l_0} [-]$$

with E the Young's modulus, σ the stress and ϵ the deformation, F the force, S the surface, l_0 the initial length and l the final length.

- The Poisson's ratio ν is defined as the lateral contraction strain in a solid divided by the longitudinal extension strain measured in a simple tension experiment [67].
- The van der Waals forces

The van der Waals forces are related to the permanent and/or induced dipoles in the molecules. A permanent dipole appears when there is an asymmetry in the electronic charges distribution within a molecule. An induced dipole appears when an electric field is applied. The van der Waals forces between atoms or/and molecules is then the sum of the Keesom force (permanent-permanent dipoles interaction), the Debye force (permanent-induced dipoles interaction) and the London dispersion (induced-induced dipoles interaction) all proportional to $1/r^6$ with r being the distance between the molecules [68].

4.2 Experimental measurement techniques

Different measurement techniques can be used to determine the adhesion energy between two surfaces. Some techniques are direct measurements, using known Young's modulus and Poisson's ratio (common values found in the literature are $E = 0.5 - 2.4$ TPa and $\nu = 0.16 - 0.165$ as seen in Appendix A). Other techniques are based on the measuring the adhesion force which will then be used as input in different conversion models to determine the adhesion energy (see Appendix B).

The adhesion energy between two materials depends on the characterization method used. Indeed energies of delamination and adhesion are different. What is expected:

$$\Gamma_{adhesion} < \Gamma_{separation}$$

4.2.1 Atomic Force Microscope Nanoindentation

The tip of the Atomic Force Microscope (AFM) measures its adhesion **force** with a substrate (see Figure 4.1).

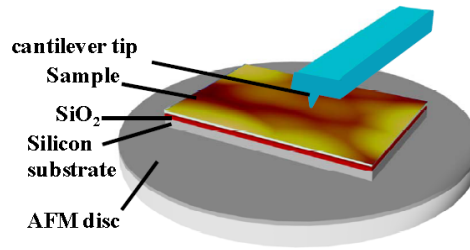


FIGURE 4.1 – Experimental setup for measuring the adhesion force between the tip and the sample [69]

Jiang et al. measured by sputtering copper onto a spherical tip its adhesion force with exfoliated graphene. They calculated the adhesion energy using a model (from Appendix B) and obtained $\Gamma_{adhesion} = 460$ mJ/m² and $\Gamma_{adhesion} = 750$ mJ/m² respectively for graphene/*SiO*₂ and graphene/*Cu* interfaces [70].

Lu et al. measured the adhesion force between a gold-coated AFM tip and *Cu* or *Cu*₂*O* surface. They found $F_{adh} \simeq 12.5$ nN for the *Cu* and $F_{adh} \simeq 10$ nN for *Cu*₂*O* [43].

Mou et al. measured the surface adhesion forces between the *Si* tip and graphene or hBN. They found $F_{adh} = 47$ nN for the graphene and $F_{adh} = 42.5$ nN for the hBN. They also observed that the force increases under illumination with a small change of 3-4 nN for hBN and graphene [69].

4.2.2 Pressurized blister test

The pressurized blister test allows to measure directly adhesion energy of thin films to their substrate. This delamination method is performed under uniform pressure. Hinkley [71] was one of the first to use this method. The principle consists of applying on one side of a suspending thin-film a fluid pressure through a circular hole in the substrate. The thin film will firstly deflect (the bulge test) then, at a critical pressure value, it will delaminate with an interfacial crack front propagation as seen in Figure 4.2 [72].

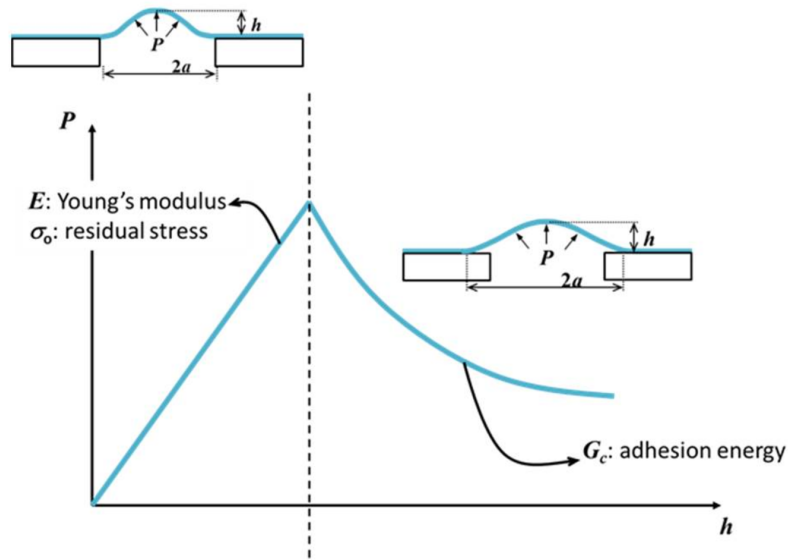


FIGURE 4.2 – Blister test principle [72]

This simple model helps to determine the following relationship between the pressure p and the central deflection of a thin film h [73].

$$h = \frac{pa^4}{64D}, \text{ with } D = \frac{Et^3}{12(1-\nu^2)}$$

with E the Young's modulus, ν the Poisson's ratio, t the thin-film thickness, D the bending stiffness and a the radius of the circular hole.

The energy release rate for delamination is

$$\Gamma_{separation} = \frac{32Dh^2}{a^4}$$

Cao et al. performed their measurement at room temperature and reported that the adhesion energy or steady-state toughness of graphene CVD on copper is 510 mJ/m^2 [73].

Koenig et al. measured that the adhesion energy between exfoliated graphene and SiO_2 is $450 \pm 20 \text{ mJ/m}^2$ [74].

Boddeti et al. obtained as adhesion energy for graphene exfoliated on top of SiO_2 a value of $140 \pm 40 \text{ mJ/m}^2$. They modified the method by starting with an annular blister [75].

4.2.3 Nano-scratch method

Das et al. proposed a new method to measure the adhesion force between graphene and its substrate using nano-scratch (see Figure 4.3). A 200nm-thick probe starts on the substrate and goes through the graphene membrane tearing it along a 15 μm scratch length. The lateral force required to tear off the graphene layer from the substrate is measured and defined as the adhesion force between the graphene and the substrate. The area under the lateral force vs. displacement curve is calculated in order to estimate the separation energy between graphene and copper, that was equal to 12750 mJ/m^2 [76].

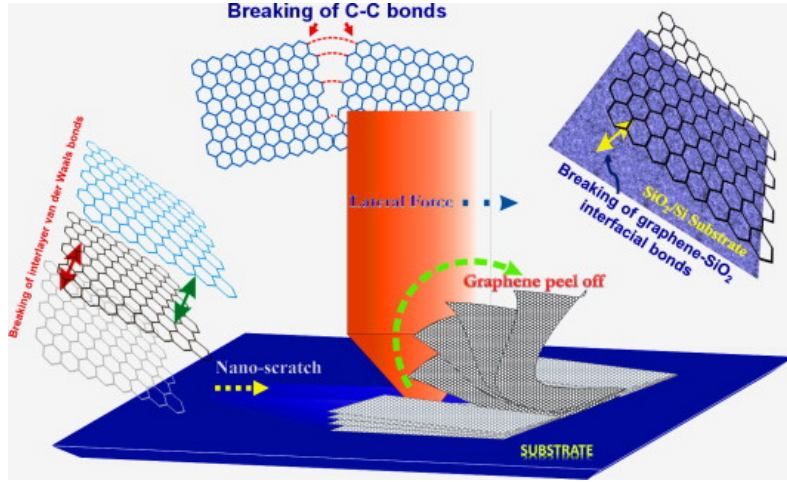


FIGURE 4.3 – Mechanism of nano-scratch technique using a nano-indenter [76]

4.2.4 Scatter nanoparticles

By intercalating nanoparticles between graphene and silicon as seen in Figure 4.4, Zong measured that the adhesion energy is equal to 151 mJ/m^2 .

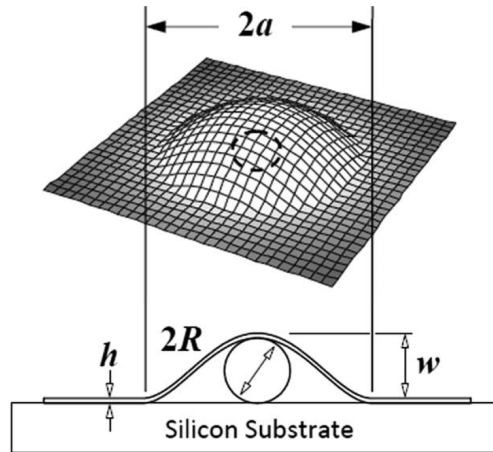


FIGURE 4.4 – Sketch of blister [77]

Gold or silver nanoparticles are spread randomly on the silicon substrate then after drying, an exfoliation of graphene is done on Si . Adhesion energy can be calculated by

$$\Gamma_{\text{adhesion}} = (1/16)Eh\left(\frac{w}{a}\right)^4$$

with E the Young's modulus, a the contracted blister radius at equilibrium and w the central blister displacement.

4.2.5 Double Cantilever Beam

The double cantilever beam (DCB) method is a mechanical delamination process as seen in Figure 4.5.

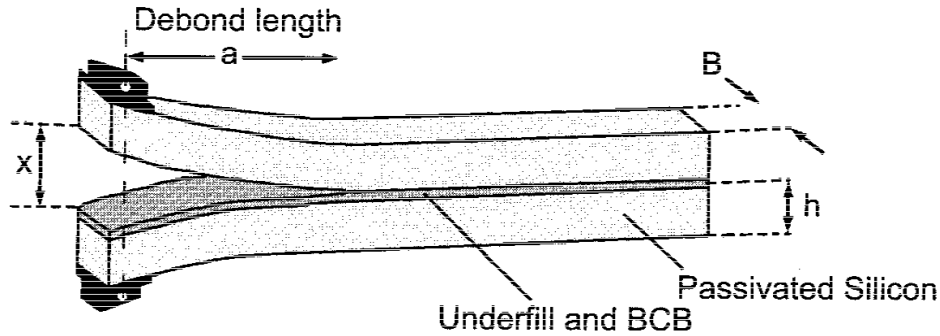


FIGURE 4.5 – Double cantilever beam method [78]

The separation energy can be calculated as follows:

$$\Gamma_{separation} = \frac{12P_c^2 a^2}{E' B^2 h^3} \left(1 + 0.64 \frac{h}{a}\right)^2$$

with P_c the critical load while cracking starts, a the crack length, B the specimen thickness, h the beam height, E' the plain-strain modulus of the beam ($E' = E/(1 - \nu^2)$ with ν the Poisson's ratio and E the Young's modulus).

The debond length at the interface can be determined either under an optical microscope or by the measurement of the elastic compliance du/dP :

$$a = \left(\frac{du}{dP}\right)^{\frac{1}{3}} \left(\frac{BE'h^3}{8}\right)^{\frac{1}{3}} - 0.64h$$

with u the total displacement of the beam ends.

Yoon et al. reported the separation energy of graphene as-grown on copper to be $720 \pm 70 \text{ mJ/m}^2$. The graphene delaminated itself from copper and not from epoxy only when the displacement rate was higher than $5 \mu\text{m/s}$. This method allows the copper substrate to be reused [59].

Na et al. showed that delamination of the graphene CVD off its copper substrate depends on the separation rate. After stacking epoxy on top of the graphene flake, when the separation rate is higher than $5 \mu\text{m/s}$, the delamination occurs along the graphene/copper interface (it still works at $254 \mu\text{m/s}$). The separation energy measured between copper foil and graphene is 6000 mJ/m^2 and between epoxy and graphene is 3400 mJ/m^2 [79].

Na et al. delaminated graphene on thin film of copper with a delamination rate of 20, 34 and $42 \mu\text{m/s}$. At higher speed, this operation did not work anymore. They measured a separation energy for Gr/Cu thin film equal to 1540 mJ/m^2 [80].

4.3 Simulations

The adhesion energy can also be determined by theory/simulation with Density Functional Theory (DFT) or from Molecular Dynamics method (MD).

4.3.1 Density Functional Theory

Density functional theory (DFT) is a quantum modelling method used in different domains to study the electronic structure of large systems. It allows the determination of the electronic properties of a system by using functional of the electron density function.

Gao et al. calculated by DFT with dispersion corrections that the adhesion energy between graphene and SiO_2 is equal to 240 mJ/m^2 [81].

Luo et al. calculated by DFT simulation that the adhesion energy for Gr/Cu_2O is equal to 354 mJ/m^2 and Gr/Cu is equal to 536 mJ/m^2 [62].

4.3.2 Molecular dynamics method

Molecular dynamics (MD) is an *Ab initio* method that allows to simulate experiments and then to calculate the adhesion energy.

Wang et al. simulated the structural transformation of 2 graphene sheets when filled by gas molecules using a numerical method [82].

4.4 Measurements and theoretical values

4.4.1 Non-numerical data

Copper vs oxidized copper

Birringer et al. reported, in 2012, that the adhesion to an oxidized or oxygen-rich Cu film is significantly lower than the adhesion of the same barrier to a clean, reduced Cu surface [83].

Lu et al. measured, in 2012, that the adhesion force at the interface Cu/gold was bigger than Cu_2O /gold [43]. The following assumption can be made:

$$\Gamma_{SLG/Cu_{oxidized}} < \Gamma_{SLG/Cu}$$

The orientation of the grain of copper has an impact on its surface energy γ . The higher the surface energy, the higher the adhesion force between graphene and copper [84, 43]:

$$\gamma_{Cu(111)} < \gamma_{Cu(100)} < \gamma_{Cu(110)} < \gamma_{Cu(124)}$$

$$\Gamma_{SLG/Cu(111)} < \Gamma_{SLG/Cu(100)} < \Gamma_{SLG/Cu(110)} < \Gamma_{SLG/Cu(124)}$$

Akgul et al. measured, in 2014, the surface energy for different types of oxidation [85]:

$$\gamma_{Cu_2O} < \gamma_{CuO} < \gamma_{Cu(OH)_2}$$

hBN vs graphene

San et al., Geim et al. and Bjorkman et al., between 2012 and 2014, assumed that the adhesion between hBN and graphene was caused by the forces of van der Waals [86, 87, 88].

Later, in 2016, Akinwande et al. in their review said that a value of adhesion energy greater than 1 J/m^2 cannot be attributed to van der Waals interactions alone [89].

SiO_2 vs polymer

Scharfenberg et al. proposed, in 2012, that [90]:

$$\Gamma_{SLG/\text{SiO}_2} \leq \Gamma_{SLG/PDMS}$$

The interaction between graphene and SiO_2/Si is relatively weak (van der Waals forces) and the interaction between graphene and PDMS is relative strong where substrate induced pre-strain in the graphene layer is observed. For graphene embedded on the PDMS substrate, the more flexible the substrate, the weaker the interaction between PDMS and graphene [91].

The higher the glass transition temperature T_g for polymer, the stronger the adhesion due to their high molecular mobility. $T_g = 100^\circ\text{C}$ for PMMA and $T_g = -120^\circ\text{C}$ for PDMS [45].

$$\Gamma_{SLG/PDMS} < \Gamma_{SLG/PMMA}$$

4.4.2 Numerical data

References	Material	γ [mJ/m ²]
van Engers, 2017 [92]	SLG	115
	FewLG	119
Buckley, 1969 [93]	Cu(111)	2499
	Cu(100)	2892
Ferguson, 2016 [94]	SLG	35-115
Soon, 2007 [95]	Cu(111)	785
	Cu(100)	1073 - 1570
Various authors, 2007 [96]	PMMA	41.1
	PDMS	19.8

TABLE 4.1 – Values of surface energy (γ) for different materials from literature

References	Substrate	$\Gamma_{SLG/Substrate}$ [mJ/m ²]	Measurement Techniques
Luo, 2017[62]	$Cu_{(foil)}$	536	Density Functional Theory §4.3.1
Na, 2015 [79]	$Cu_{(foil)}$	6000	Double Cantilever Beam §4.2.5
Das, 2013 [76]	$Cu_{(foil)}$	12750	Nano-scratch Method §4.2.3
Cao, 2014[73]	$Cu_{(film)}$	510	Pressurized Blister Test §4.2.2
Yoon, 2012 [59]	$Cu_{(film)}$	720 ± 70	Double Cantilever Beam §4.2.5
Jiang, 2015 [70]	$Cu_{(film)}$	750	AFM Nano-indentation §4.2.1
Na, 2016 [80]	$Cu_{(film)}$	1540	Double Cantilever Beam §4.2.5
Luo, 2017 [62]	$Cu_2O_{(foil)}$	354	Density Functional Theory §4.3.1
Boddeti, 2013 [75]	SiO_2	140 ± 40	Pressurized Blister Test §4.2.2
Boddeti, 2013 [97]	SiO_2	240	Pressurized Blister Test §4.2.2
Gao, 2014 [81]	SiO_2	240	Density Functional Theory §4.3.1
Koenig, 2011 [74]	SiO_2	450 ± 20	Pressurized Blister Test §4.2.2
Jiang, 2015 [70]	SiO_2	460	AFM Nano-indentation §4.2.1
Zong, 2010 [77]	Si	151	Scatter Nanoparticles §4.2.4
Geim, 2013 [87]	hBN	160	<i>Not mentioned</i>
Bjorkman, 2012 [88]	hBN	320	<i>Not mentioned</i>
Na, 2015 [79]	<i>Epoxy</i>	3400	Double Cantilever Beam §4.2.5

TABLE 4.2 – Values of some adhesion/separation energy between a single layer of graphene (SLG) and a substrate

Chapter 5

Electronic mobility

Graphene is a material with unique electronic transport properties such as high Fermi velocity, excellent carrier mobility, and high carrier saturation velocity. Hole and electron mobilities are nearly identical.

Interaction between the graphene and its substrate is one of the main factors determining its electronic quality. One of the most used substrate is silicon oxide (SiO_2). Due to its roughness, the presence of trapped charges, and the surface phonons, it significantly limits the mobility of charge carriers in devices [5, 53]. The highest mobility reached with SiO_2 is in the range of 15 000 (at room temperature) to 25 000 cm^2/Vs (at $T = 1.6K$).

A straightforward way of reducing the graphene perturbations is to remove the substrate and suspend the graphene flake. After an annealing treatment to remove the residual impurities, this method allows mobility until 230 000 cm^2/Vs (at $T = 5K$) but the mechanical instability of such devices due to the large applied voltages, do not allow high charge carrier densities [53].

A recent improvement in graphene device electronic quality was the use of hexagonal boron nitride (hBN) as substrate material. Single layer of hBN crystals are atomically flat and contain a very low amount of charged impurities [5]. These properties allow electronic mobility to reach 140 000 (at room temperature) to 275 000 cm^2/Vs (at $T = 4.2K$).

This chapter presents the standard device fabrication of a Hall bar which is used to calculate the electronic mobility through current-voltage measurements. It follows with a review of the relation between the electronic mobility of the graphene with its Raman spectrum. It finishes with the presentation of some main values on electronic mobility.

5.1 Standard device fabrication

Once the graphene is transferred on hBN or encapsulated, the sample is spin-coated with polymethylmethacrylate (PMMA) photoresistant. An electron beam lithography is realized to define a Hall bar structure of graphene, and oxygen plasma etching is used to eliminate the unnecessary parts. Another electron beam lithography is achieved to define the electrode pattern, and metal deposition is done across this electron beam evaporation. A standard metal lift-off is achieved and the as-fabricated devices are annealed in a hydrogen atmosphere (400°C for 1 hour) to remove the residues and improve the graphene-electrode contact [63].

5.2 Mobility measurements

Mobility (μ) can be determined by the Drude's model [8, 98]:

$$\sigma = \mu n e [S]$$

$$\mu = \frac{\sigma}{n e} [cm^2/Vs]$$

With σ the electrical conductivity, n the sheet carrier density and e the elementary charge (1.602×10^{-19} C). The sheet carrier density, n , in function of V_G , can easily be found assuming parallel plate capacitor geometry.

$$n = C_G(V_G - V_{Dirac})/e [cm^{-2}]$$

where V_G is the voltage applied at the gate, V_{Dirac} is the Dirac voltage, e is the elementary charge and C_G is the capacitance per area of the parallel plate capacitance. This capacitance is given by:

$$C_G = \frac{\epsilon_{ox}}{t_{ox}} [F/cm^2]$$

with ϵ_{ox} the oxide permittivity and t_{ox} the oxide thickness. The electrical conductivity can also be measured and obtained by the relation:

$$\sigma = \frac{L}{W} \frac{I_d}{V_d} [S]$$

with I_d and V_d correspond to the current and voltage of the drain. So the mobility is given by:

$$\mu = \frac{1}{n e} \frac{L}{W} \frac{I_d}{V_d} [cm^2/Vs]$$

So, an easy method using an Hall bar (Figure 5.1) to calculate the mobility of a graphene layer is the I_{DS} - V_G measurement. It consists of applying a voltage at the gate of the device and measuring the current that flows from the drain to the source. As mentioned in section 1.1, this type of curve gives information on the graphene characteristics as its Dirac voltage and so the type of doping (n or p-type). Using these measurements, the carrier density n , the conductivity σ and the mobility μ of the graphene can be approximated.

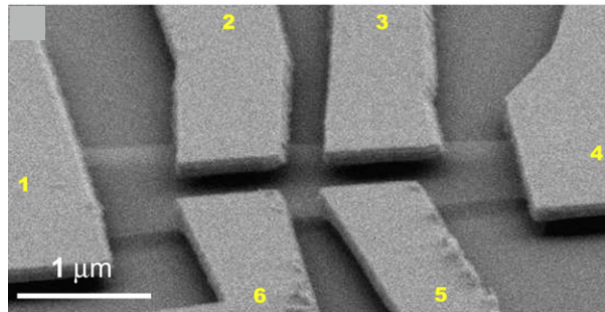


FIGURE 5.1 – Hall bar used to extract mobility [99]

5.3 Relation between the mobility and the Raman

An analysis of the charge carrier mobility of a graphene flake can be done with a Raman spectroscopy.

In 2012, Lee et al. showed that the strain variation had an impact on the position of the 2D and G peak of the Raman spectrum of a graphene flake, modifying its electronic properties [100].

Zhao et al. demonstrated the correlation between the shape of the G and 2D peaks of a graphene flake and the surface roughness of its substrate. If the surface roughness increases, a shift to the left for the G and 2D peak is observed (Figure 5.2a) and the Full Width at Half Maximum of the two peaks also increases (Figure 5.2b) [101].

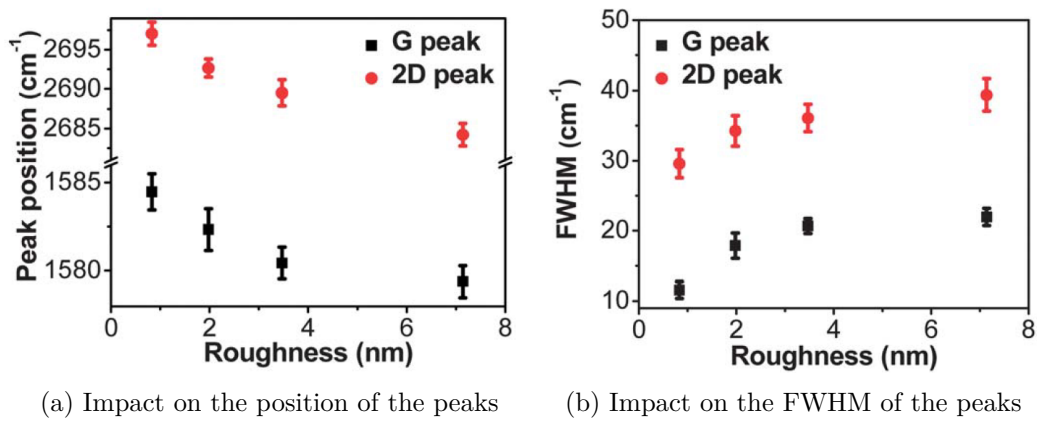


FIGURE 5.2 – Dependence of the G and 2D peaks with the surface roughness of the substrate [101]

On the other hand, Leon et al. observed, as a dependence of the substrate on the Raman peaks of graphene flakes, that the downshift of the D peak appears larger for a hBN substrate than for a SiO_2 substrate due to less doping of the graphene. They also showed that the position of the 2D peak depends on the substrate (as seen in Figure 5.3). However, they observed, as Zhao et al., that the FWHM(G) was sharper for graphene on hBN than on SiO_2 [54].

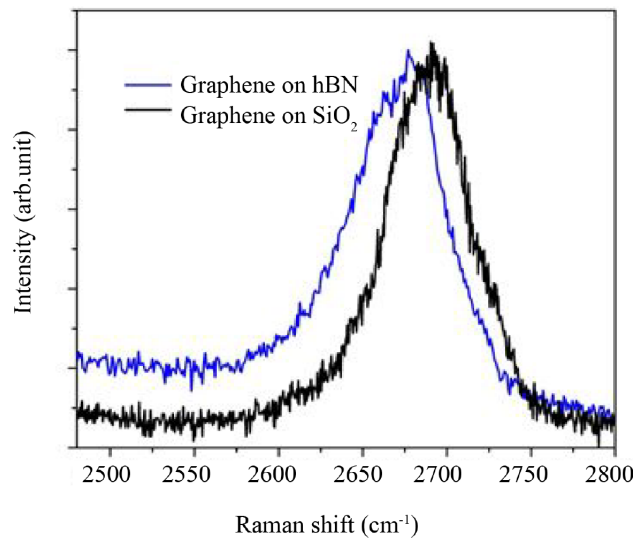


FIGURE 5.3 – Comparison of Raman 2D peak for Graphene on hBN and SiO_2 [54]

As seen in Figure 5.4, there is a dependence between $\bar{\Gamma}_{2D}$, the FWHM(2D) of a flake of graphene on different substrates (SiO_2 or hBN), and the mobility. The sharper the peak, the higher the mobility.

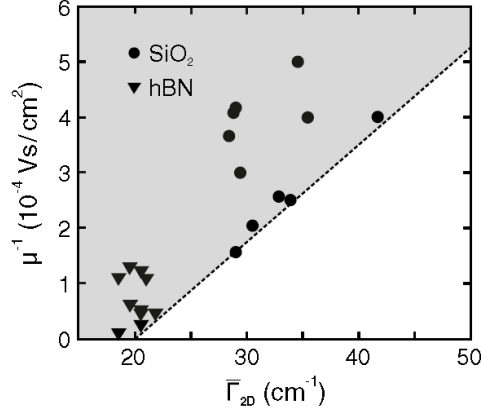


FIGURE 5.4 – Link between the inverse mobility and the average FWHM of the Raman 2D peak $\bar{\Gamma}_{2D}$ for graphene flakes on different substrates (SiO_2 and hBN) [102]

Banszerus et al. found that the substrate induces a strain variation in the graphene. Similarly to the results of Zhao et al., the 2D peak broadens with the surface roughness due to the strain variation. Using Lee's vector decomposition model, Banszerus et al. showed the correlation between the position of the G and D peaks and the graphene strain due to its substrate (Figure 5.5). They determined from this model the effect of the strain on the quality. The higher the strain variations, the higher is the limitation of the charge carrier mobility [103].

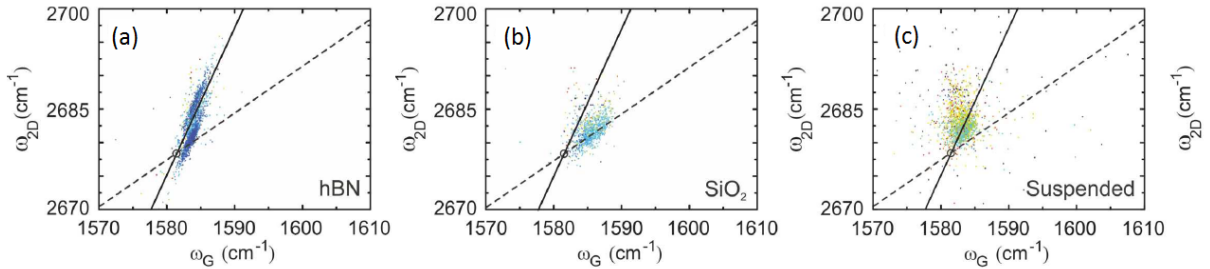


FIGURE 5.5 – Vector decomposition model [103]

5.4 Numerical data

Here after some other interesting values from the literature (see Table 5.1 for dry transfer results and Table 5.2 for wet transfer results).

The mobility is temperature dependent, so the best results are measured at low temperature. Results show a rise from $125\,000\text{ cm}^2/Vs$ at room temperature to $275\,000\text{ cm}^2/Vs$ at $T = 4.2K$ for a dry-transferred graphene on hBN [104].

As mentioned before, the values obtained for the electronic mobility for graphene on hBN are much higher than on SiO_2 . Results show a rise from $25\,000\text{ cm}^2/Vs$ on SiO_2 to $45\,000\text{ cm}^2/Vs$ on hBN for wet transfer at $T = 1.6K$ and from $15\,000\text{ cm}^2/Vs$ to $37\,000\text{ cm}^2/Vs$ at room temperature [105, 56].

An annealing of the Hall bar is performed to remove residues from PMMA. The mobility is much higher after with $230\,000\text{ cm}^2/Vs$ than before with $28\,000\text{ cm}^2/Vs$ at $T = 5K$ for suspended graphene [99]. Contacts can be degraded by the annealing step in Ar/H_2 [54] .

Annealed suspended graphene and dry transferred graphene on hBN achieved similar results (annealing is no more necessary if the sample is encapsulated in a dry manner [44]).

The length of the channel has an impact on the mobility. An increase of the channel length will increase the mobility. This mobility saturates to a constant value at channel length of several micrometers (between 5 and $10\text{ }\mu m$) [98, 106].

References	Length [μm]	SLG	Dielectric	$\mu\text{ [cm}^2/Vs]$	$T_{measure}\text{ [K]}$	Annealing
Petrone, 2012 [105]	5	CVD	SiO_2	25000	1.6	after
	5		hBN	45000	1.6	after
Calado, 2014 [107]	2.5	CVD	hBN	17000	room	after
				29000	4	after
Tombros, 2011 [108]	4	EXF	none	37000	77	before
				600000	77	after
Bolotin, 2008 [109]	2	EXF	none	120000	240	after
				28000	5	before
				170000	5	after
Bolotin, 2008 [99]	4	EXF	none	28000	5	before
				230000	5	after
Du, 2008 [110]	0.5	EXF	none	120000	100	after
				185000	20	after

TABLE 5.1 – Electronic mobility for wet transfer method (using etchants)

References	Length [μm]	Graphene	Dielectric	μ [cm^2/Vs]	$T_{measure}$ [K]
Dean, 2010 [52]	10	EXF	hBN	40000	room
				60000	2
Zomer, 2011 [53]	10	EXF	hBN	40000	room
Zomer, 2012 [104]	20	EXF	hBN	125000	room
				275000	4.2
Dean, 2012 [111]	4	EXF	hBN	35000	room
Wang, 2013 [49]	15	EXF	2 hBN	140000	room
Banszerus, 2015 [65]	12	CVD	hBN	100000	room
				110000	1.6
Banszerus, 2016 [106]	20	CVD	hBN	130000	room
				147000	1.8
Tien, 2016 [56]		EXF	SiO_2	15000	room
			hBN	37000	room
			2 hBN	100000	room

TABLE 5.2 – Electronic mobility for dry transfer method

Part II

Materials and methods

Chapter 6

Materials

This section describes the general process of fabrication for graphene structure on thin films, hBN or other supports used during the transfer process.

6.1 Silicon dioxide fabrication process

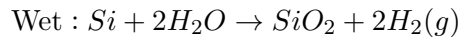
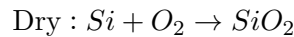
Si/SiO_2 is used in this work for two different reasons. The first one is because of its insulating electrical properties. The second one is because its special light reflection allows a flake of graphene to be seen for some specific thickness of SiO_2 . Indeed, direct observation of the transfer is a real help in the process regarding the time consumption. 300 nm and 90 to 100 nm are the most suitable thicknesses for the visual detection of the graphene [112]. In this work, a 90nm-thick wet oxide is used. This thickness will ensure the integrity of the oxide during the fabrication process.

6.1.1 Sample cleaning

The silicon is previously cleaned to ensure its purity throughout the process. First, the sample is soaked in deionized water and dived in a piranha solution (mixture of H_2SO_4 and H_2O_2) to remove the visible residues. The rest of the cleaning can be divided in three steps. An organic cleaning is realized with a base-peroxide mixture to remove organic residues. This treatment results in the formation of a thin silicon dioxide layer ($\approx 10 \text{ \AA}$) on the silicon surface. The second step removes this thin oxide layer and a fraction of ionic contaminant by soaking the sample in an aqueous solution of hydrofluoric acid ($\approx 1 : 50$) for a few seconds [113]. The third step will remove the remaining traces of metallic (ionic) contaminants by immersing the sample in a HCl solution. Finally, the wafer is rinsed and dried.

6.1.2 SiO_2 growth

The first step of the fabrication process is the growth of a SiO_2 layer on the silicon wafer. There are two SiO_2 growth methods: dry and wet oxidation, depending on whether dry oxygen or water vapor is used. Wet oxidation has a fast oxidation rate compared to dry oxidation but dry has a high density and best quality oxide. Therefore, wet oxidation is used when the electrical and chemical properties of the film are not critical. The global reactions for dry and wet oxidation process are the following:



6.2 Graphene fabrication process

6.2.1 Graphene CVD

Chemical vapor deposition is the method used for the synthesis of the graphene in this work. Copper is used as growth substrate and methane as carbon source. Two types of catalysts are used for this work: thin Cu film and bulk Cu foil. Graphene synthesis was performed in *Winfab* clean room by Benjamin Huet.

The process consists in the two following steps. First, the temperature is brought to $T_1 \approx 600^\circ\text{C}$ and H_2 is introduced in the furnace chamber during 20 min. This elevation of temperature will anneal the copper and increase its domain size. Then, the temperature is brought to $T_2 \approx 1000^\circ\text{C}$ and methane (CH_4) is introduced in the chamber during 5 to 30 min. During this step, hydrogen is pumped into the chamber to control the nucleation density and the shape of the graphene flakes.

6.2.2 Copper Oxidation

Copper (foil or thin film) is the substrate used in all of the CVD growth processes realized in the scope of this work. A quick oxidation of the copper (around 30 seconds at ambient temperature) can be done to bring to light the graphene structure on the substrate. But a deeper oxidation can also go further and reduce the adhesion energy between the graphene and the substrate.

The two most common oxides of copper are Cu_2O and CuO . CuO has a black color and Cu_2O a brownish-red color [85]. The dominant oxide at low temperature (between 70°C and 130°C) is Cu_2O , as Cu_3O_2 is only formed between 150°C and 250°C and at high temperature (more than 250°C) it is CuO [114, 115]. Additional oxides may appear such as Cu_xO (with $x > 2$) and $Cu(OH)_2$. The thickness and composition of the oxide scale is a function of temperature and humidity. Two categories of copper oxidation exist: wet or dry.

Copper dry oxidation

Dry oxidation is the easiest to execute. The foil is placed on a hot plate in a humid ambient air.

During the first minutes, for low temperature, the oxide rate is linear and reaches a thickness of 0.13 and 1.22 nm for the respective temperatures of 30 and 90°C . When the thickness of the oxide film reaches several nanometers, the oxidation slows down drastically. The growth can be estimated by a logarithmic rate and can reach a thickness from 0.74 to 23 nm for 30 and 90°C after 20 hours. The dominant oxide is Cu_2O due to the significant activation enthalpy of the oxidation of Cu to CuO [116].

At intermediate and high temperatures, oxide thickness often follows a linear rate during the first minutes followed by a cubic rate law. Unlike the oxidized films obtained at low temperature, the oxide film contains both Cu_2O and CuO . The oxide growth rate is very high with a thickness of 1500 nm reached after 60 seconds at 400°C [114]. The relative air humidity affects also the oxidation rate. More the air is humid, greater is the oxide thickness.

Copper wet oxidation

The graphene/copper stack is laid in a water container and placed on a hotplate.

For low temperature, oxide thickness is thicker for wet than for dry oxidation. At the same condition, oxide thickness can reach 795 nm after 60 seconds at 30°C against 616 nm for

dry oxidation [114]. However at higher temperature, oxide thickness is similar for wet or dry oxidation.

Graphene impact

The thermal annealing process is an easy detection technique to optically characterize graphene growth and domains directly on its copper substrate. The process lasts a little time (e.g. 6 minutes for 160°C) at high temperature (graphene is thermally stable and impermeable below 400 °C). It is enough to transform the copper to copper oxides while keeping graphene and graphene-covered copper intact [32]. The higher the temperature used for the thermal annealing process, the less time it takes to visually detect the graphene.

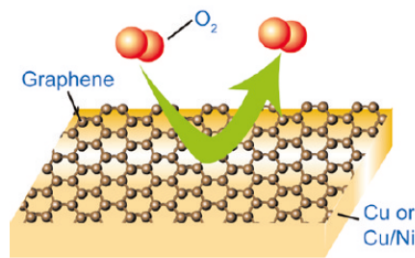


FIGURE 6.1 – Natural protection of graphene against oxidation [117]

If the process is performed during a longer time, the oxidation will spread also on the graphene-covered copper starting from the edges and defects on graphene islands, and then gradually progress under the graphene layer. The grain orientation of the copper under graphene has also an impact on the rate of the oxidation. Indeed, the higher the surface energy between graphene and Cu(iii), the better the protection against oxidation. The graphene/Cu(124) is relatively inert to ambient oxidation, while the oxidation rate below graphene/Cu(111) is higher than under the graphene/Cu(100) [43].

It remains mandatory to keep an eye on the possible oxidation and/or hydrogenation of the graphene sample [118].

6.3 hBN fabrication process

6.3.1 hBN exfoliation

The exfoliation of hBN is made between two adhesive pieces of PDMS. To favour the flake adhesion, an oxygen-plasma treatment of the PDMS can be performed before exfoliation [48]. Visually, the contrast between the substrate and the flakes helps to determine the number of layers of hBN. Greater the contrast is, greater the number of layers will be [24]. The thickness of the hBN is determined due to a trade-off between further fabrication process issues and a decrease in the electronic mobility. The hBN flake must not be too thick otherwise thicker metallic contacts will be needed, leading to lift-off problems. The hBN flake must be at least 5 nm-thick otherwise graphene will still be sensitive to roughness and charged impurities from the underlying SiO_2 [119].

6.3.2 Polymers

Microfluidic devices reduce cost and simplify manufacturing procedures. Here are used amorphous polymers as PDMS and PMMA. These transparent materials are rigid below their glass transition temperature (T_g) and soft and flexible after [120].

PDMS

PDMS or polydimethylsiloxane is a silicon based polymer which has hyperelastic properties, high transparency, flexibility, low cost, robustness, and good resistance to heat and chemicals. PDMS is one of the most widely used polymer for the contact lenses application. Moreover, it allows oxygen and carbon dioxide to diffuse through it [121]. Thermal decomposition which starts at about 200°C can meaningfully reduced mechanical strength of the PDMS layer [122]. PDMS used in this work is GelPak and so allows a fast and easy use. The glass transition temperature for the PDMS is $T_g = -120^\circ\text{C}$ [45].

PMMA

PMMA or polymethyl-methacrylate (also known as plexiglas) is a transparent thermoplastic. PMMA is found in a liquid form and will be diluted with anisole to obtain a 2, 4 or 6% solution. The surface to be covered with PMMA is placed on a spin coater where vacuum is maintained between the spinning part and the surface to ensure its positioning. A drop of diluted PMMA is deposited on the flake and after the spin-coating (between 1000 and 4000 rpm), a PMMA layer of uniform thickness is distributed on the surface. This thickness is function of the percentage of the solution of PMMA and of the rotational speed. The melting point of PMMA is about 130 to 140°C and its boiling temperature is at 200°C. The glass transition temperature for the PMMA is $T_g = 100^\circ\text{C}$ [45]. Moreover, PMMA is more rigid than PDMS and can be dissolved by organic solvents. [121].

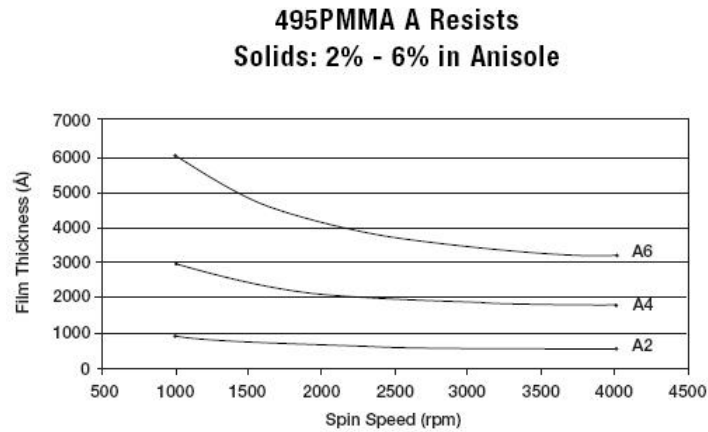


FIGURE 6.2 – Influence of PMMA percentage and spin speed on the film thickness [123]

Chapter 7

Tools and Characterization methods

This chapter presents different devices used during the experiments. It focuses on their utilization and on interesting results found in literature.

7.1 Micromanipulator

Micromanipulators are used to align the flakes of graphene and hBN and ensure a good contact, alignment and orientation between these two layers during the transfer.

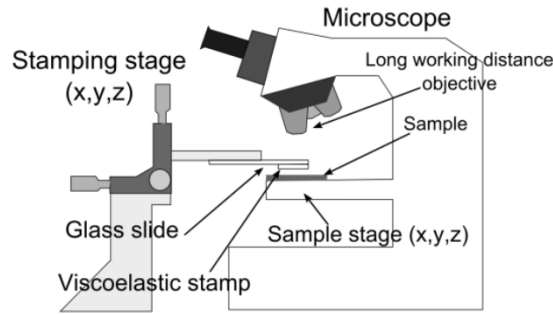


FIGURE 7.1 – Experimental setup use for the dry transfer [55]

The general setup is composed of one optical microscope with a long focal distance (≈ 15 cm), one X-Y-Z micromanipulator and one rotational and X-Y adjustment(Figure 7.1). The two movable decks of the Thorlabs micromanipulators have a full 13 mm course of travel in the two or three orthogonal directions. A 3D view of the manipulator is given in Figure 7.2. A small thermocouple is included in the device to heat up the samples.

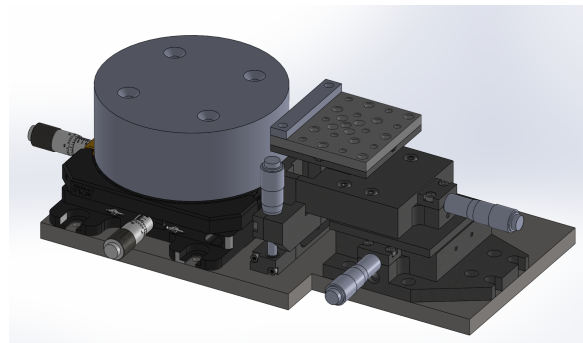


FIGURE 7.2 – Micromanipulators Thorlabs [124]

7.2 Raman spectroscopy

The Raman spectroscopy is a non-destructive technique used to characterize and observe the molecular composition of materials. It is based on the Raman effect, i.e. a small fraction of scattered radiation is slightly different from the frequency of the monochromatic incident radiation. This phenomena had been discovered in 1928. The laser light (red or green) interacts with molecular vibrations, resulting in an up- or down-shifting of the energy of the laser photons. This shift (Δw) is given by :

$$\Delta w = \left(\frac{1}{\lambda_0} - \frac{1}{\lambda_1} \right)$$

with λ_0 is the excitation wavelength and λ_1 the Raman wavelength. This shift will give information about the vibrational modes and the material itself. A sample is illuminated with a laser beam (red or green) and the illuminated spot from the radiation is collected in a lens and sent through a monochromator.

Much of this scattered radiation has a frequency which is equal to the frequency of incident radiation and constitutes Rayleigh scattering. Only a small fraction of scattered radiation has a frequency different from the frequency of incident radiation and constitutes Raman scattering [125]. The Rayleigh scattering is filtered out by a filter and the Raman scattering is dispersed onto a detector [126].

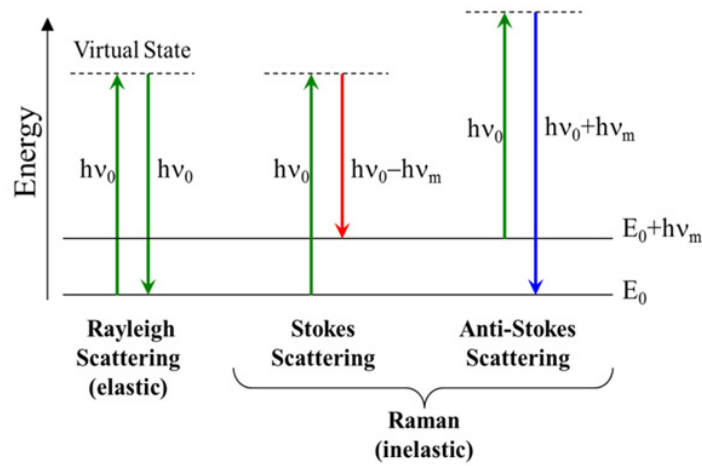


FIGURE 7.3 – Diagram representing quantum energy transitions for Rayleigh and Raman scattering. Energy is given by $E=h\nu$, where h is Planck's constant and ν is the frequency of the radiation. [127]

7.2.1 Raman spectrum of graphene on SiO_2

The Raman spectrum of graphene contains a lot of informations like its atomic structure or its electronic properties thanks to its zero-band gap making all wavelengths of incident radiation resonant. Structural damages and chemical modifications from the previous preparation or transfer process are easily identifiable [118].

Three common peaks have been reported in the Raman spectrum of graphene monolayer: the D, G and G' (or 2D) band. The most significant features are the G and G' peaks appearing, respectively, at 1582 cm^{-1} (graphite) and at about 2700 cm^{-1} (see Figure 7.4). A third peak, the so-called disorder-induced D-band, appears for disordered sample or at the edge of a graphene sample at about half of the frequency of the G' band around 1350 cm^{-1} (*using laser excitation at 2.41 eV) [128].

The width, the intensity (I) and the position of the Raman peaks vary with the graphene electronic and structural properties [118].

The 2D peak of a single layer of graphene (SLG) has a FWHM equal to $25\text{-}35\text{ cm}^{-1}$ and can be fitted to a single Lorentzian. The 2D peak broadens and up-shifts while the number of graphene layer increases [129]. An estimation of the number of layers can also be done with the intensity ratio of 2D and G peaks (I_{2D}/I_G). The ratio decreases while the number of layers increases. It is also used to estimate the doping level of graphene. The ratio increases while the doping level decreases. An intense 2D-peak will be present for a high quality of the graphene.

The D peak is directly associated with the presence of defects. The intensity ratio of D and G (I_D/I_G) decreases while the quality increases. The D-peak will be absent for graphene of high quality [41].

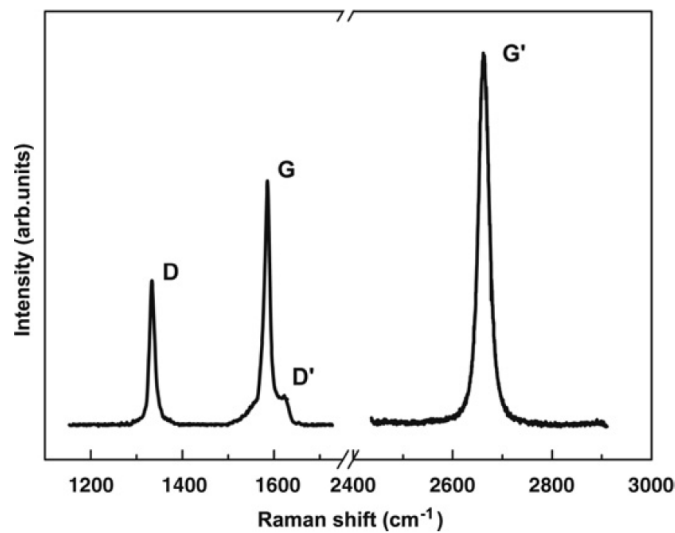
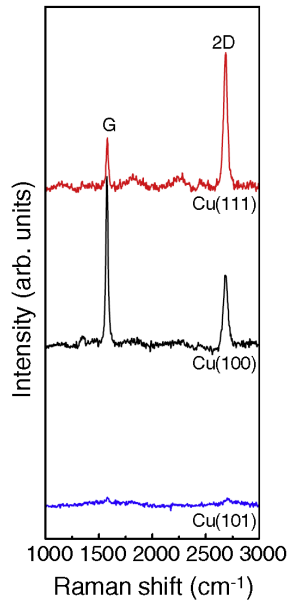


FIGURE 7.4 – Raman spectrum of graphene [128]

	Peaks D - G - 2D [cm^{-1}]	I_{2D}/I_G	FWHM(2D) [cm^{-1}]
SLG	1350 - 1582 - 2700	>2	25-35

TABLE 7.1 – Peaks, Peaks ratio and FWHM(2D) for SLG [43] [41]

7.2.2 Raman spectrum of graphene on copper



The orientation of the copper grain has an impact on the quality of the as-grown graphene (Figure 7.5 and Table 7.2).

The preferential growth of graphene is on Cu(111). The growth of SLG is rapidly depressed on Cu(100) and Cu(110). No peaks of graphene will be found on Cu(101) [131].

	I_{2D}/I_G	2D width [cm^{-1}]
As-grown SLG/Cu(100)	1.5-2	40-50
As-grown SLG/Cu(111)	1-1.5	40-50

TABLE 7.2 – Peaks ratio of graphene on copper [43]

FIGURE 7.5 – Raman spectrum of graphene on copper [130]

7.2.3 Raman spectrum of graphene on oxidized copper

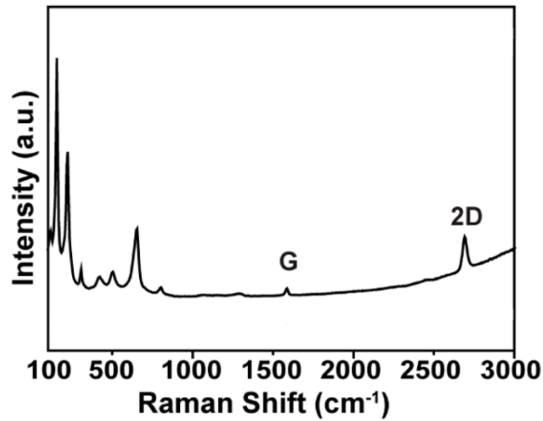


FIGURE 7.6 – Raman spectrum of oxidized copper with graphene [62]

Oxidation may produce different types of oxidized copper (see vibrational peaks in Tab. 7.3 and Figure 7.6). It is difficult to detect Cu_3O_2 [132].

	Peaks [cm^{-1}]
Cuprous oxide Cu_2O	109-150-217-644
Copper hydroxyde $\text{Cu}(\text{OH})_2$	799
Cupric oxide CuO	298-412-497
Copper(III) oxide Cu_3O_2	1135

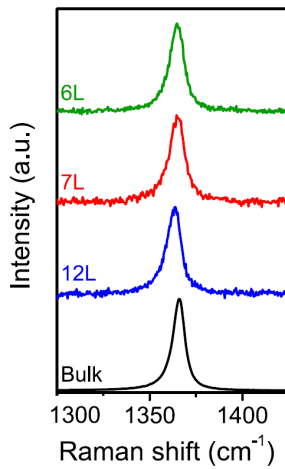
TABLE 7.3 – Peaks of oxidized copper [62, 117, 85, 115]

The orientation of the grain has also a huge impact on its oxidation. The higher the surface energy of the grain, the higher the adhesion energy between graphene and copper, the better the protection against further oxidation [84, 43]:

$$\gamma_{\text{Cu}(111)} < \gamma_{\text{Cu}(100)} < \gamma_{\text{Cu}(110)} < \gamma_{\text{Cu}(124)}$$

Peaks could appear if an hydrogenation (1130 cm^{-1} and 1450 cm^{-1}) or an oxidation (1150 cm^{-1}) of the graphene takes place [133].

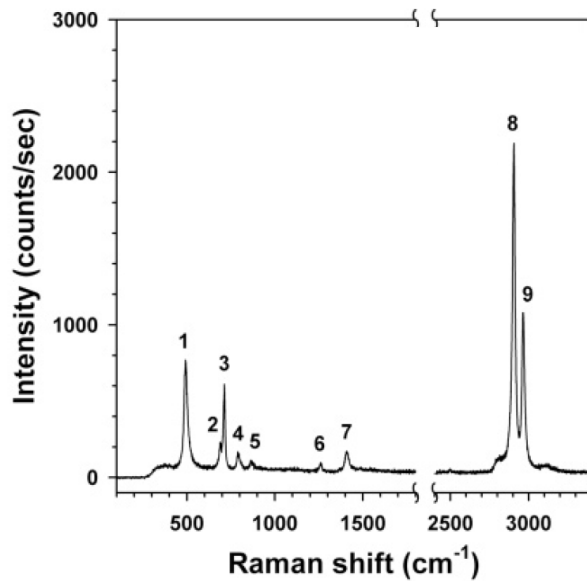
7.2.4 Raman spectrum of hBN



In Figure 7.7, a peak is observed due to the in-plane atom vibrations at 1366 cm^{-1} with $\text{FWHM} \leq 10\text{ cm}^{-1}$ for exfoliated hBN. The less the number of layers of hBN the more the peak tends to 1350 cm^{-1} [134].

FIGURE 7.7 – Raman spectrum of hBN [134]

7.2.5 Raman spectrum of PDMS



In Figure 7.8, the numbers next to the vibrational peaks represent [135]:

- (1) Si-O-Si symmetric stretching (488 cm^{-1}),
- (2) Si-CH₃ symmetric rocking (687 cm^{-1}),
- (3) Si-C symmetric stretching (708 cm^{-1}),
- (4) CH₃ asymmetric rocking + Si-C asymmetric stretching (787 cm^{-1}),
- (5) CH₃ symmetric rocking (862 cm^{-1}),
- (6) CH₃ symmetric bending (1262 cm^{-1}),
- (7) CH₃ asymmetric bending (1412 cm^{-1}),
- (8) CH₃ symmetric stretching (2907 cm^{-1}), and
- (9) CH₃ asymmetric stretching (2965 cm^{-1}).

FIGURE 7.8 – Raman spectrum of PDMS [135]

7.2.6 Raman spectrum of PMMA

In Figure 7.9, the most intense vibrational peak is due to [136]:

C–H stretching at 2957 cm^{-1} ,
with a FWHM = 42.44 cm^{-1} .

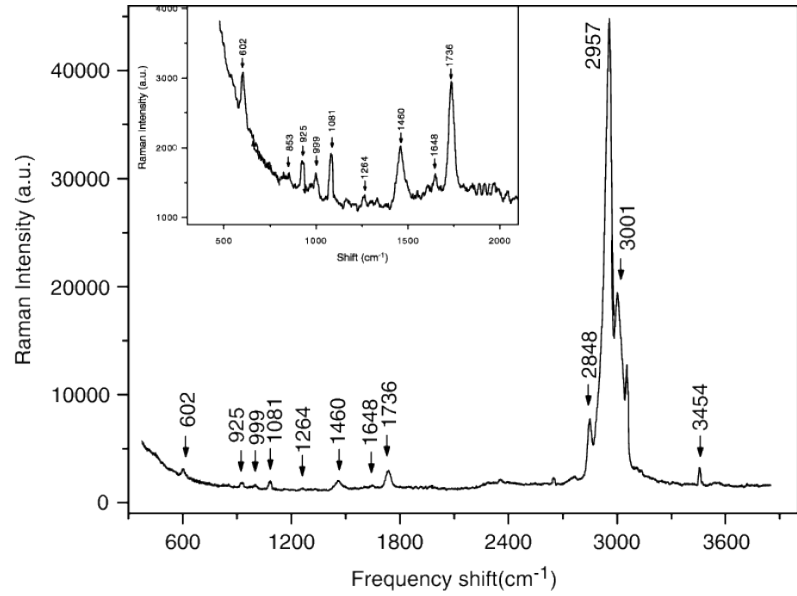


FIGURE 7.9 – Raman spectrum of PMMA [136]

7.2.7 Raman spectrum of SiO_2/Si

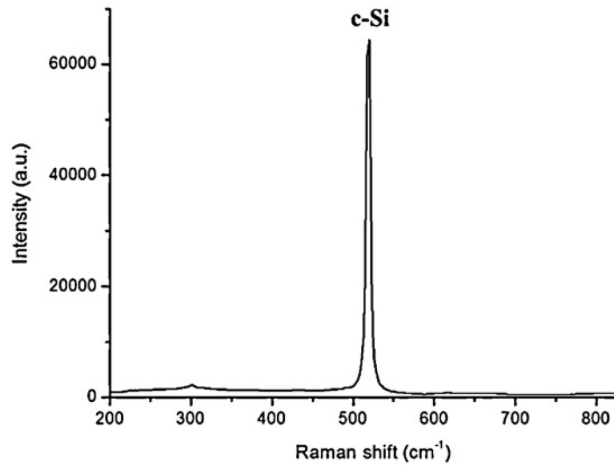


FIGURE 7.10 – Raman spectrum of silicon wafer [137]

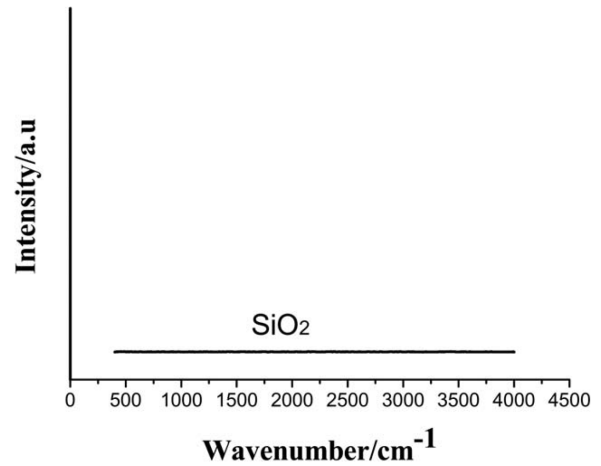


FIGURE 7.11 – Raman spectrum of SiO_2 [138]

In Figure 7.10, a solitary sharp peak is observed at 520 cm^{-1} for the silicon wafer [137].

In Figure 7.11, there is no apparent peak, only a straight line for SiO_2 [138].

Part III

Results

Chapter 8

Experimental results

In this chapter, the results of the different experiments are detailed. The graphene available was CVD graphene and the hBN flakes were mechanically exfoliated in the *Winfab* facility. The extraction of graphene from its copper growth substrate in order to transfer it on hBN has been performed either by etching the Cu away or by mechanical delamination. As the utilization of the etchant leaves too many residues on the graphene for its further use, delamination techniques were approached. In order to facilitate the isolation process, the first approach was to minimize the adhesion energy between graphene and copper and the procedure proposed in this work is by (dry or wet) oxidation of the graphene-covered copper. Ways to maximize the adhesion between graphene and its transfer mask (hBN/polymer or polymer) are also proposed.

Two different methods of transfer of CVD graphene on hBN were then tested. In the first, intermediate polymer layer delaminates the graphene flake from its copper substrate. Then the graphene is put into contact with a hBN flake. In the second one, the hBN flake delaminates the graphene flake from its copper substrate. Then the graphene is put into contact with another hBN to be encapsulated. To carry out these experiments, the preparation of the different stacks before contact has been carefully studied.

This chapter presents first the minimization of the energy between copper and graphene by thermal oxidation while keeping a good quality of the graphene. Then it describes the preparation of the transfer masks to guarantee its useful transparency. It follows with a comparison of the quality of wet-transferred graphene on two different substrates, by two different wet transfer methods (with PMMA or PDMS). It ends with the detailed process of the two dry methods tested with the transfer results.

To verify that a transfer takes place, several types of detection are used. The first one is the visual detection but since graphene is transparent, it is hard to see it. To circumvent this, tricks are used such as oxidizing the copper/graphene or placing graphene on SiO_2 . The second detection used is the RAMAN spectroscopy. It determines with more accuracy the different layers of our sample. Dry oxidation and 90 nm of silicon dioxide thickness are chosen for the quality and the visual aspect.

8.1 Copper oxidation

One of the main characteristics that influences the peeling of the graphene from the copper is the adhesion energy between copper substrate and graphene. One goal of this research is thus to decrease this adhesion energy to facilitate the delamination of the graphene. As proposed in section 4.4.1, the relation between adhesion energy of graphene and oxidized copper or non-oxidized copper can be written as follows:

$$\Gamma_{SLG/Cu_{oxidized}} < \Gamma_{SLG/Cu}$$

Two types of oxidation have been realized in the scope of this work: dry oxidation and wet oxidation. Dry oxidation is performed in air, in clean room, directly on a hotplate during various periods of time and at different temperatures. For the wet oxidation, the sample is placed on the surface of water in a sealed container. The container is then placed on a hotplate during various periods of time and at different temperatures. During the whole process, the quality of the graphene is checked. An optimum is found to maintain a good graphene quality but with the highest amount of oxidized copper, by choosing the good temperature/time ratio.

In Figure 8.1, the specimen is oxidized during 30 seconds at high temperature (max. 400°C as mentioned in section 6.2.2) to bring to light the graphene structures on the copper substrate without damaging the quality of the graphene. The main Raman peaks expected for the copper oxides are presented in Table 8.1 (as mentioned in section 7.2.3).

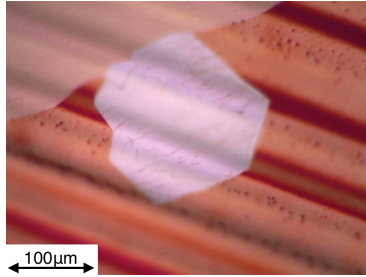


FIGURE 8.1 – Microscopic view of CVD graphene flake on copper foil after 30s of dry oxidation

	Peaks [cm^{-1}]
Cu_2O	109 - 150 - 217 - 644
$\text{Cu}(\text{OH})_2$	799
CuO	298 - 412 - 497

TABLE 8.1 – Main Raman peaks for oxidized copper

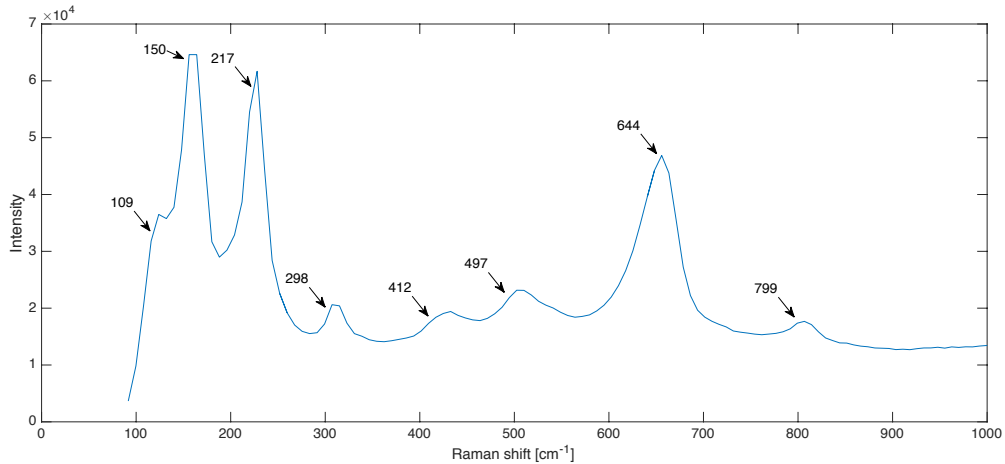


FIGURE 8.2 – Typical Raman spectrum of oxidized copper

Figure 8.2 shows a typical Raman spectrum of oxidized copper. All the peaks in relation with Cu_2O (109, 150, 217 and 644 cm^{-1}), $Cu(OH)_2$ (799 cm^{-1}) and CuO (298, 412 and 497 cm^{-1}) are present. Raman spectroscopy will so allow to determine which type of oxide is present on copper.

8.1.1 Dry Oxidation Cu/Gr CVD thin film

A dry oxidation of a copper thin film covered by graphene is realized on a hotplate in clean room at 250°C . The microscopic view of the flake (Figure 8.3) shows that, after an oxidation of 30s, the oxidized copper regions are easily visible under the optical microscope and allow unequivocal identification of areas where graphene is present or not. The oxidized copper has a red color and the graphene flakes have a white shade. After an oxidation of 3 hours, the copper begins to softly darken and after 7 hours, graphene flakes have a dark shade and the copper is burgundy.

Oxidation at 250°C

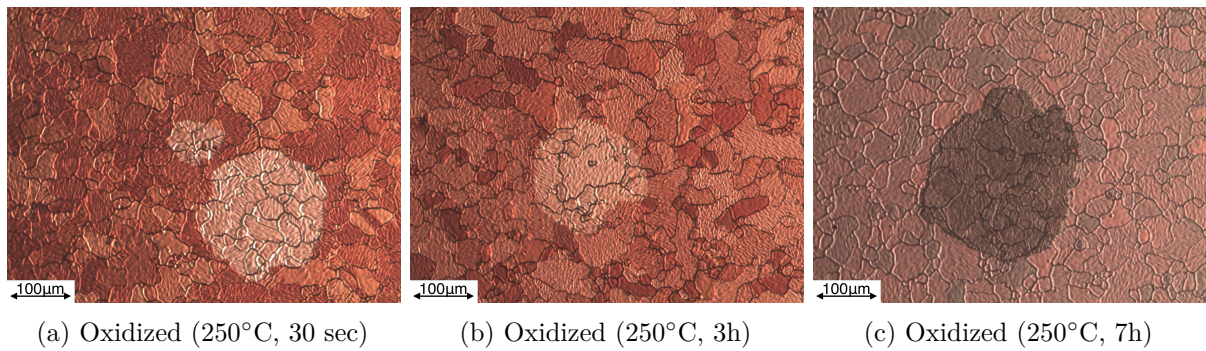


FIGURE 8.3 – Microscopic view of CVD graphene flake on copper thin film after dry oxidation

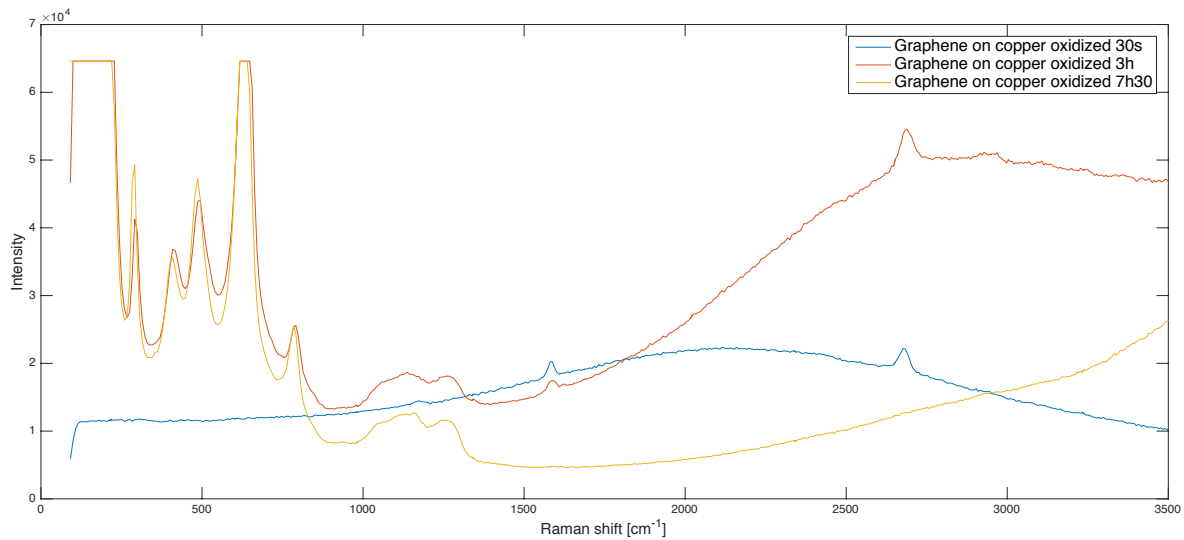


FIGURE 8.4 – Raman spectrum of oxidized copper/graphene after 30s, 3h, 7h30 at 250°C

Raman spectroscopy was performed on graphene flakes of the different oxidized copper to evaluate the evolution of its quality in function of time at a temperature of 250°C . Measurements were made at the center of the flake. All the graphene flakes are from the same CVD process and on the same copper thin film. The results obtained are shown in Figure 8.4. Values of the three

main peaks of graphene (D, G and 2D) and the relation between them are given in table 8.2. For all the flakes, the intensity of the D peak is negligible, that shows a high structural quality of the flake. The position of the two other peaks (G and 2D) is nearly unchanged even after 3 hours oxidation and their localization is close to the one expected (1582 cm^{-1} for G and 2700 cm^{-1} for 2D [41]). The general curve of the spectrum is the signature of copper. It can be seen that the copper oxide peaks appear on the 3-hour spectrum. All peaks corresponding with Cu_2O , $\text{Cu}(\text{OH})_2$ and CuO are present. It means that the copper under the graphene flake contains all of these oxides. These peaks are still present for a time of oxidation of 7h30.

Peaks	D [cm^{-1}]	G [cm^{-1}]	2D [cm^{-1}]	I_{2D}/I_G	FWHM(2D) [cm^{-1}]
30s oxidized	-	1582	2685	1.75	27
3h oxidized	-	1588	2689	3.1	33
7h30 oxidized	-	-	-	-	-

TABLE 8.2 – Peaks, Peaks ratio and FWHM(2D) for a dry oxidation during 30s, 3h and 7h30 at 250°C

Ratio between 2D and G peaks of 30s and 3h oxidized graphene are always greater than 1.7 meaning a relatively good quality for the graphene after 3 hours of oxidation. Nevertheless, after 7h30, the two expected graphene (G and 2D) peaks are absent in the spectrum and this seems to indicate that graphene is no more present on the copper and thus that this oxidation time is too high.

Evolution of the copper oxidation into the same graphene flake

Dry oxidation was performed during 3 hours on a copper thin film where graphene have been CVD grown. Two different graphene flakes present on the same thin film are presented on Figure 8.5. The first one (Figure 8.5a) has a dark shade everywhere while the other one (Figure 8.5b) is both black and white. This difference of color into the same graphene flake is the result of a variation of the oxidation state of copper under the flake.

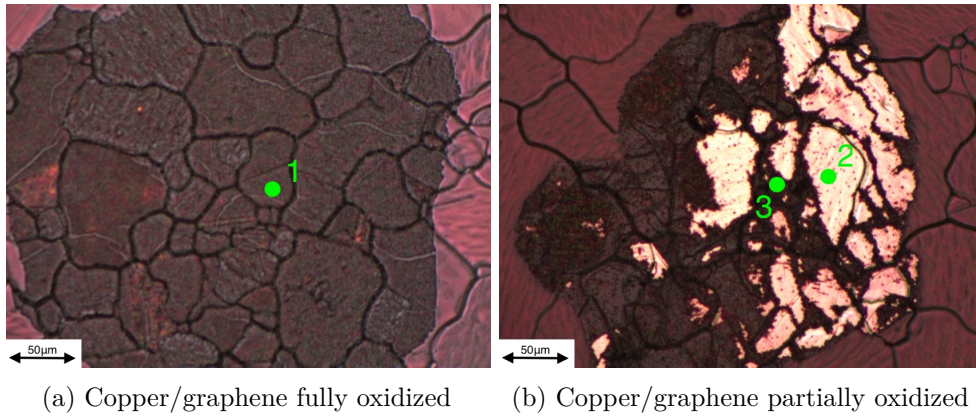


FIGURE 8.5 – Microscopic view of CVD graphene flake on copper thin film after 3h of dry oxidation at 250°C

Raman spectroscopy at different points of the flake is realized to associate a color with the progress of the oxidation. It can be seen on the Raman spectrum (Figure 8.6) that the points 1 and 3 display similar curves, with all the copper oxide peaks (between 0 and 1000 cm^{-1}), while point 2 (located in the white area of graphene flake) does not display these peaks, indicating that the underlying copper has not been oxidized.

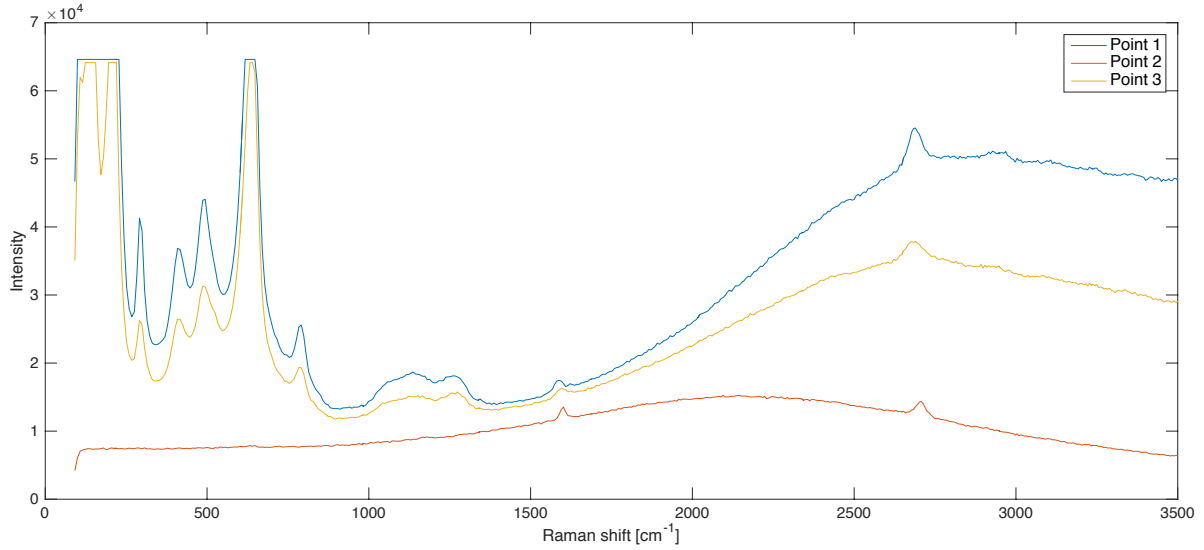


FIGURE 8.6 – Raman spectrum of oxidized copper/graphene after 3 hours at 250°C at different points

8.1.2 Dry Oxidation Cu/Gr CVD foil

As for the dry oxidation for thin film, dry oxidation for copper foil is performed on a hotplate in cleanroom at a certain temperature.

The main copper oxides expected from literature for low ($T < 130^\circ\text{C}$), medium ($150^\circ\text{C} < T < 250^\circ\text{C}$) and high ($T > 250^\circ\text{C}$) oxidation temperatures are respectively Cu_2O , Cu_3O_2 and CuO (as mentioned in section 6.2.2).

From section 4.4.1, the type of oxidized copper has an impact on the adhesion with the graphene, as shown by the following relation for surface energy:

$$\gamma_{\text{Cu}_2\text{O}} < \gamma_{\text{CuO}} < \gamma_{\text{Cu}(\text{OH})_2}$$

During the experiments, oxidation under the graphene flake appeared quicker at high temperature (200°C) and slower at low temperature (50°C) (from Table 8.3).

The start time is the time needed for the copper under graphene to oxidize (for 50 % of the sample), the stop time is the duration after which the peaks of graphene disappear or when the quality of the graphene decreases. The type of oxidized copper depends on the temperature and the humidity (dry).

Temperature [°C]	Start [hour]	Stop [hour]	Type of oxidized copper
200	24	39	Cu_2O , $\text{Cu}(\text{OH})_2$, CuO
120	-	-	Cu_3O_2^*
60	48	70	Cu_2O
50	60	-	Cu_2O

TABLE 8.3 – Oxidation dependence on temperature and time *From literature

The size of the flakes has also an impact on the time needed for the oxidation under the flake. If the size is too big, the oxidation will not have enough time to spread everywhere under

the flake before the degradation of the graphene by the heat takes place. The evolution of the oxidation under the flake will be explained below in this section.

Foils are corrugated and under high temperature, it may happen that the edges of the sample rise up. The temperature is slightly different from one place to another on the same sample. The temperature that is defined is the temperature of the hotplate.

As seen for the copper thin film, under the same flake, different evolution of the oxidation appears. It is no longer due to the corrugated state since thin film stays flat under temperature. A study is performed, in this section, on the impact of the orientation of the grain of copper.

Oxidation at 200°C

After placing the sample on a hotplate at 200 °C during 39 hours, some flakes of graphene are half-white, half-brown (as seen in Fig 8.7).

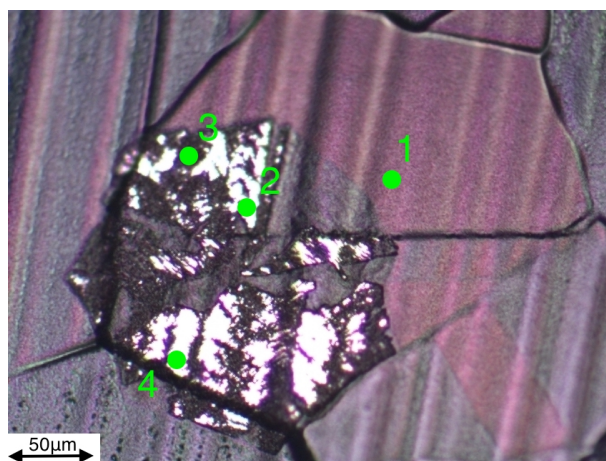


FIGURE 8.7 – Microscopic view of CVD graphene flake on copper after 39h of dry oxidation at 200°C

Four Raman spectrums for different parts of the graphene flake and the copper are given below (see Figure 8.8). The blue line (point 1) is for the oxidized copper non-covered by graphene. The red and purple lines (point 2 and 4) are for the white parts of the graphene on two different copper grain. The yellow line (point 3) is for a black/brown part.

On the spectrum, one can directly observe that not all lines have peaks below 1000 cm^{-1} , related to copper oxides, and that one of the spectrum of the graphene flake has no peaks between 1000 and 3000 cm^{-1} , related to the graphene. So, those results show that on the same flake, some parts do not have anymore the peaks of graphene while some others do not have the peaks of oxidized copper yet.

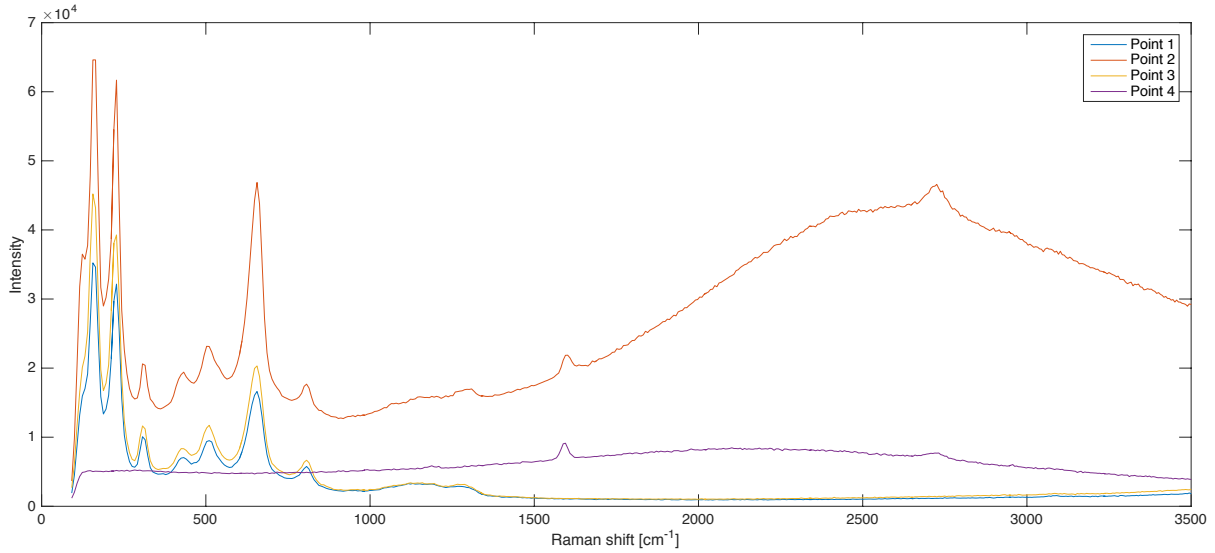


FIGURE 8.8 – Raman spectrum 39h of dry oxidation at 200°C

The peaks and ratio are listed in the Table 8.4 here below to allow a better understanding of the different parts.

Peaks	D [cm^{-1}]	G [cm^{-1}]	2D [cm^{-1}]	I_{2D}/I_G	FWHM(2D) [cm^{-1}]
Point 1 (copper)	-	-	-	-	-
Point 2 (white graphene)	1280	1598	2725	1.75	82
Point 3 (black graphene)	-	-	-	-	-
Point 4 (white graphene)	-	1590	2715	0.3	50

TABLE 8.4 – Peaks, ratio peaks and FWHM(2D) for the dry oxidation during 39h at 200°C

The graphene is probably single layered because its FWHM(2D) ($= 50 \text{ cm}^{-1}$ at point 4) is included between 40 and 50 cm^{-1} when laying on its copper substrate (as mentioned in section 7.2.2). The ratio I_{2D}/I_G , related to the quality of the graphene, is very low for the graphene (0.3) on point 4 because of a tiny 2D peak. No presence of D-peaks related to the defects. All the peaks below 1000 cm^{-1} are from Cu_2O , $Cu(OH)_2$ and CuO . The high temperature helps the production of too many types of copper oxides. Furthermore, there is not oxidation everywhere and the quality is already decreasing. In conclusion, temperature of 200°C is considered as too high for this type of air humidity.

Oxidation at 60°C

A dry oxidation of copper at 60°C during 66 hours gives to the copper its brownish-red color (as seen in Figure 8.9) due to the presence of Cu_2O .

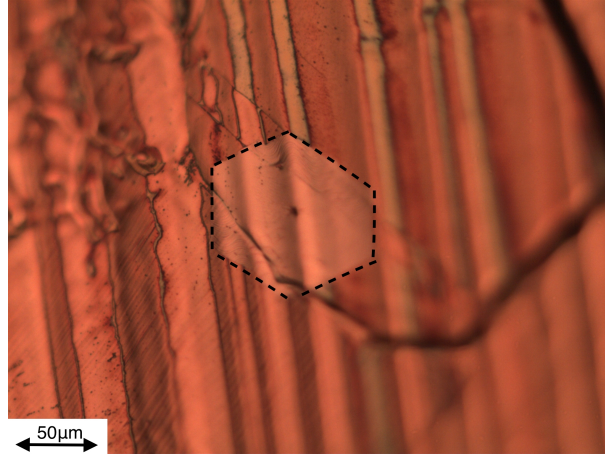


FIGURE 8.9 – Microscopic view of CVD graphene flake on copper after 66h of dry oxidation at 60°C

The results of the Raman spectrum (Figure 8.10) are given in the Table 8.5.

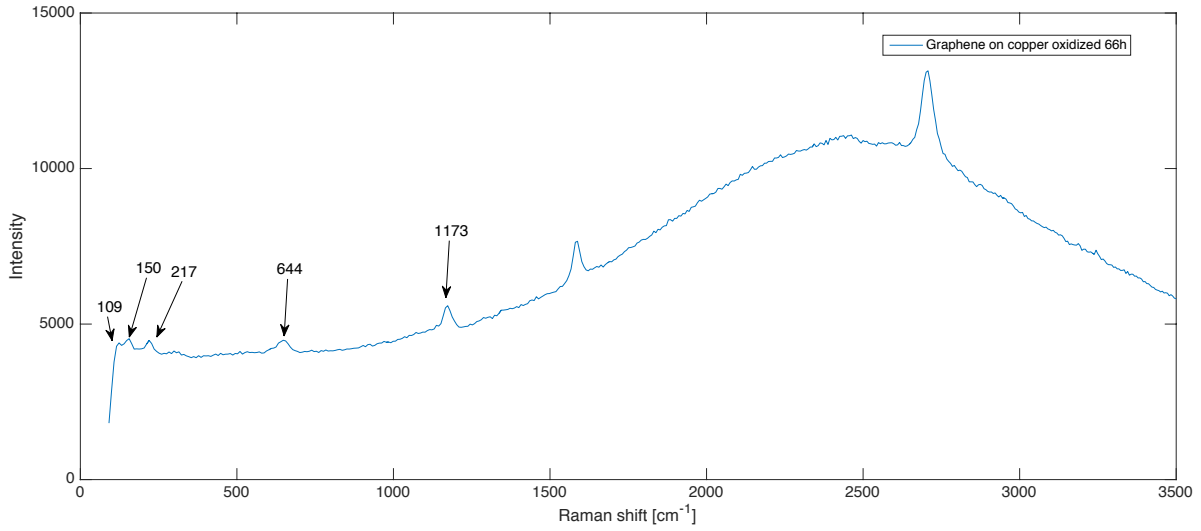


FIGURE 8.10 – Raman spectrum 66h of dry oxidation at 60 °C

Peaks	D [cm^{-1}]	G [cm^{-1}]	2D [cm^{-1}]	I_{2D}/I_G	FWHM(2D) [cm^{-1}]
Gr/Cu_{ox} (66h, 60°C)	-	1588	2707	2.6	42

TABLE 8.5 – Peaks, ratio peaks and FWHM(2D) for the dry oxidation during 66h at 60 °C

The graphene is probably single layered because its FWHM(2D) is equal to 42 cm^{-1} . After 66 hours, peaks of oxidation are visible under the whole flake. They are all from only one type of oxidized copper, Cu_2O (109, 150, 217 and 644 cm^{-1}). A peak appears next to 1150 cm^{-1} (1173) and may be interpreted as an hydrogenation of graphene (as mentioned in Section 7.2.3).

Progression of oxidation under a graphene flake at $T = 60^\circ\text{C}$ in function of time

To analyze the progression of the oxidation under a graphene flake, different Raman spectrum were realized on the same flake with different times of oxidation at a temperature of 60°C . Different points of the sample (referenced on Figure 8.11) were tested for the different times of oxidation.

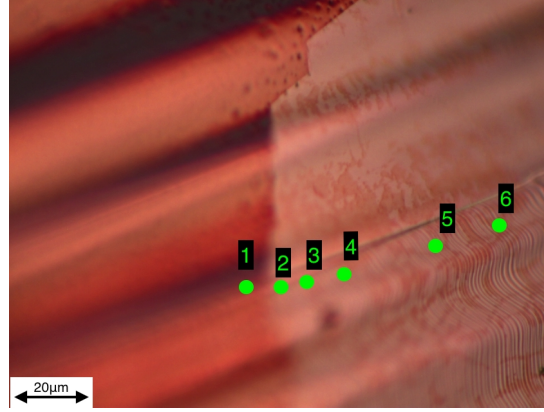


FIGURE 8.11 – Microscopic view of CVD graphene flake on copper foil after dry oxidation at 60°C

A quick oxidation of 30 seconds gives the spectrum on Figure 8.12. It can be seen that all the points (2, 3 and 4) present a G and 2D peaks at 1580 and 2700 cm^{-1} and that the ratio $I(2D/G) \approx 1.85$. D peak does not appear on these spectrum. Moreover, no copper oxide peaks are visible which seems to suggest that copper under graphene is not yet oxidized.

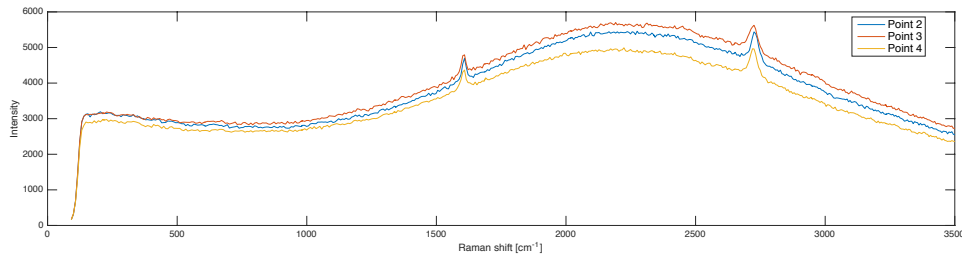


FIGURE 8.12 – After 30s of dry oxidation

A second oxidation during 16 hours is performed. Raman spectroscopy of points 2, 3 and 4 are shown on Figure 8.13. Spectrum realized on point 2 shows oxidized copper peaks contrariwise with points 3 and 4.

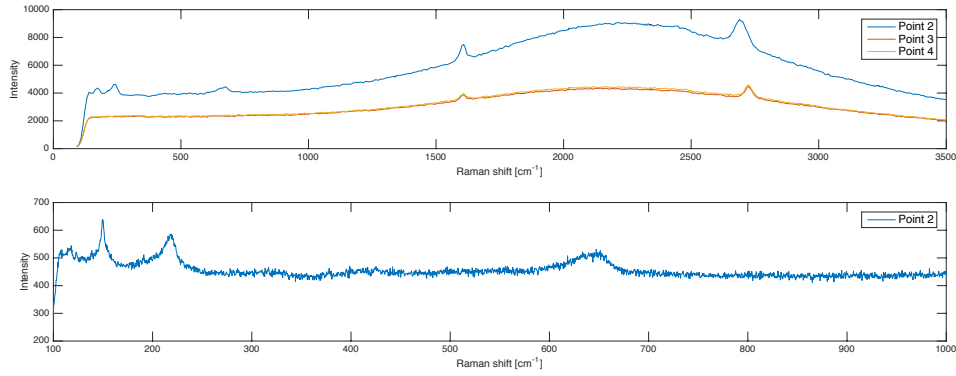


FIGURE 8.13 – After 16h of dry oxidation

Figure 8.14 shows spectrum for points 2, 3 and 4 after an oxidation of 24 hours. G and 2D peaks are still present for all the points. Copper oxidation peaks are now present for points 2 and 3. So the oxidation reaches the copper to the point 3 (at $20\ \mu m$ of the edge of the graphene island).

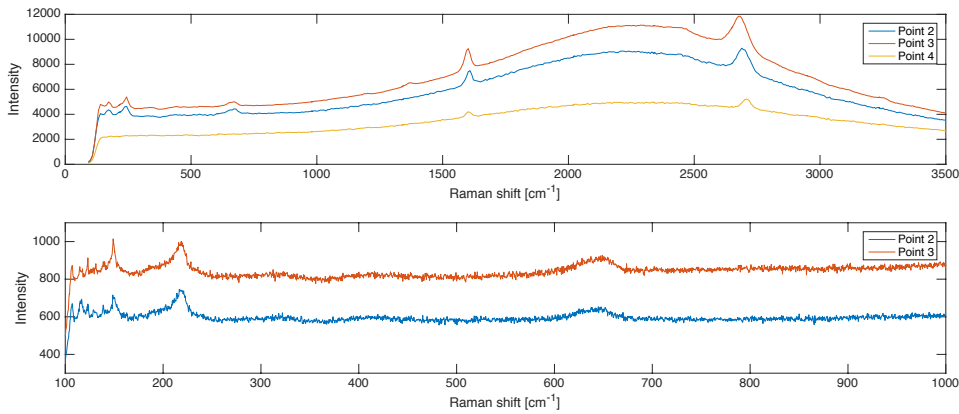


FIGURE 8.14 – After 24h of dry oxidation

After 48 hours of oxidation (Figure 8.15), all the points tested on the graphene island present copper oxidation peaks and so it can be assumed that all the copper under the graphene flake is oxidized.

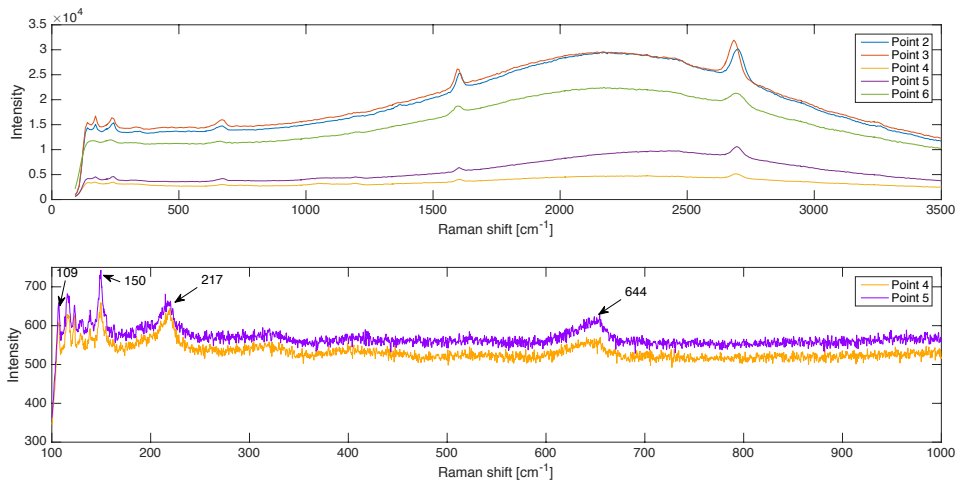


FIGURE 8.15 – After 48h of dry oxidation

All the spectrum of oxidized copper display the same peaks. On Figure 8.15, value of main peaks is presented. They are located at 109, 150, 217 and 644 cm^{-1} and so correspond to the presence of Cu_2O . Due to the relatively small temperature of oxidation, CuO peaks ($98, 412$ and 497 cm^{-1}) are not present due to the significant activation enthalpy of the oxidation to CuO .

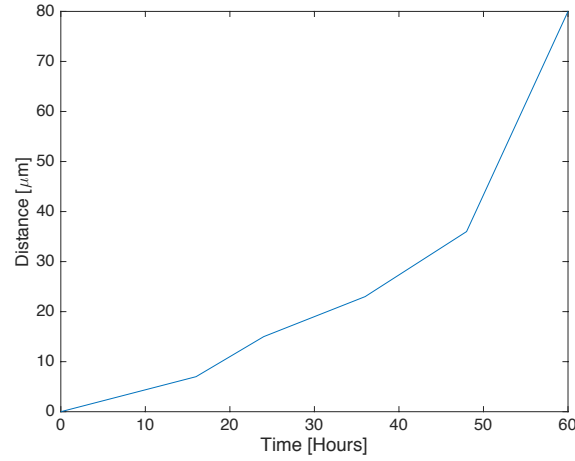


FIGURE 8.16 – Progress of copper oxidation from the edge of the flake

Figure 8.16 gives the copper oxidation progress under the graphene from the edge of the flake. Oxidation rate is about 1 to $2\text{ }\mu\text{m}$ per hour.

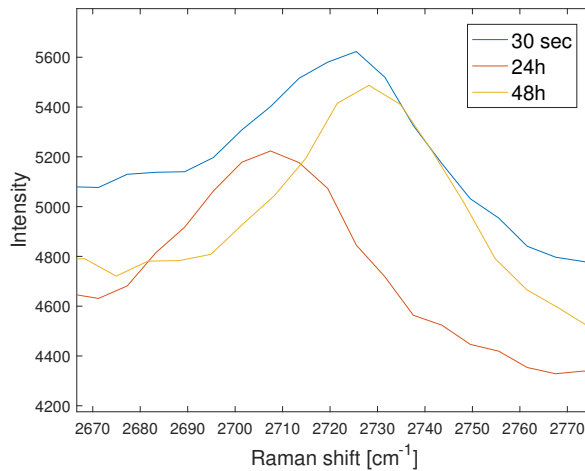


FIGURE 8.17 – Raman spectrum of graphene on oxidized copper

A more careful analysis of the 2D peaks is done in Figure 8.17 and Table 8.6. It is seen that the 2D peak shift and the FWHM(2D) shrink during the oxidation. Indeed, the oxidation induces a strain gradient in the graphene flake due to the non-uniform oxidation.

	Pos(2D) [cm^{-1}]	FWHM(2D) [cm^{-1}]
30 sec	2726	42
24h	2707	33
48h	2728	30

TABLE 8.6 – Position and FWHM of the 2D peak for dry oxidation

Impact of the grain orientation on the evolution of the oxidation

As mentioned in section 4.4.1, the surface energy of a grain of copper depends on its orientation. Knowing the following relation:

$$\gamma_{Cu(111)} < \gamma_{Cu(100)} < \gamma_{Cu(110)} < \gamma_{Cu(124)}$$

The same relation can be determined for the adhesion energy between graphene and a copper grain. The higher the surface energy, the higher the adhesion energy between graphene and copper and the better the protection against further oxidation, as shown by the following relation:

$$\Gamma_{SLG/Cu(111)} < \Gamma_{SLG/Cu(100)} < \Gamma_{SLG/Cu(110)} < \Gamma_{SLG/Cu(124)}$$

As mentioned in section 7.2.2 from Lu's research, the orientation of a grain can be determined by the ratio of the peaks I_{2D}/I_D , of the graphene flake covering it, with 1 to 1.5 for Cu(100) and 1.5 to 2 for Cu(111) and with a FWHM(2D) between 40 and 50 cm^{-1} .

As seen before, dry oxidation of copper at 60°C leaves to the copper its brownish-red color after 66 hours of oxidation but for 24 hours the color is more red or orange (as seen in Figure 8.18) also due to the presence of Cu_2O .

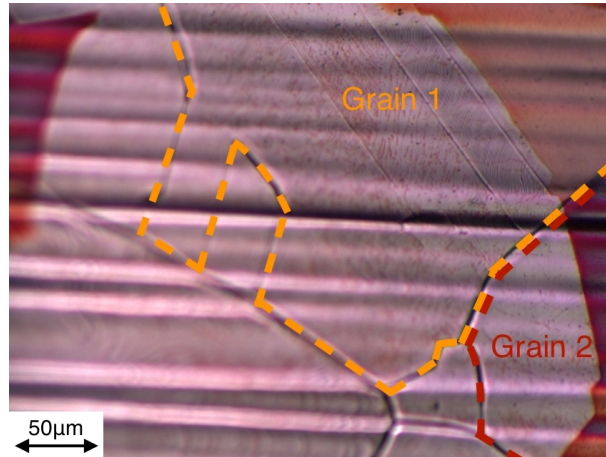


FIGURE 8.18 – Microscopic view of CVD graphene flake on copper foil after 24h of dry oxidation at 60°C

The results of the Raman spectrum (Figure 8.19) are given in the Table 8.7.

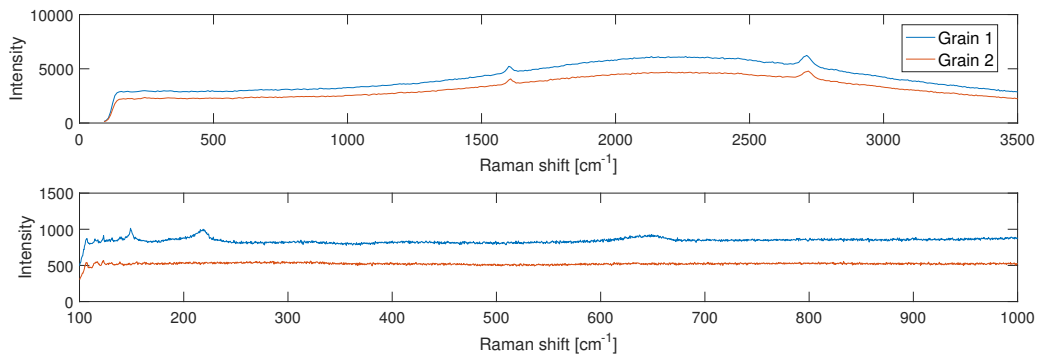


FIGURE 8.19 – Raman spectrum of graphene on copper after 24 hours at 60°C at 1 μm of the edge

Peaks	D [cm^{-1}]	G [cm^{-1}]	2D [cm^{-1}]	I_{2D}/I_G	FWHM(2D) [cm^{-1}]
24h Orange grain n°1	-	1602	2712	1.85	42
24h Red grain n°2	-	1608	2719	1.4	42

TABLE 8.7 – Peaks, Peaks ratio and FWHM(2D) for the wet oxidation

The orange grain n°1 has a ratio I_{2D}/I_G of 1.85 and is considered as a Cu(111). The red grain n°2 has a ratio of 1.4 and is considered as a Cu(100). As expected from literature, the oxidation rate is faster for the Cu(111) which has oxide peaks while the Cu(100) has none at the same distance from the edge.

8.1.3 Wet oxidation Cu/Gr CVD foil

Wet oxidation was performed in a sealed glass container filled by water placed on a hotplate. For that, firstly, the graphene/copper is deposited on the surface of the water and left to float. Then, the container is sealed to prevent the water from leaving. The temperature and time used for the oxidation are the same as those of Luo et al. [62]. They found that after 48 hours in a bath heated up to 50°C, no D peak appears while the copper is oxidized below the graphene. The only difference between their experiment and this one is that Luo et al. used a support to avoid the contact between the copper and water and especially between graphene and water.

Oxidation at 50°C

At the end of the wet oxidation, the copper/graphene is picked up from the water and then is dried either in ambient air (see Figure 8.20a and Figure 8.20b), or by a N_2 flow (see Figure 8.20c). The results show no obvious difference in the quality of the graphene after one or the other drying methods.

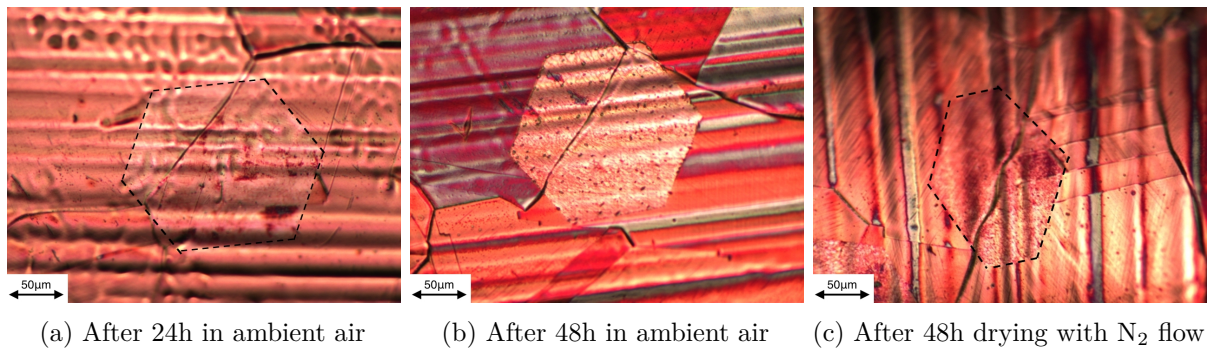


FIGURE 8.20 – Microscopic view of CVD graphene flake on copper foil after wet oxidation at 50°C

The Raman spectrum of four different graphene flakes is given below (see Figure 8.21). The blue line is for the graphene on oxidized copper from 24 hours of wet oxidation. The red, yellow and purple is for the graphene on oxidized copper from 48 hours of wet oxidation.

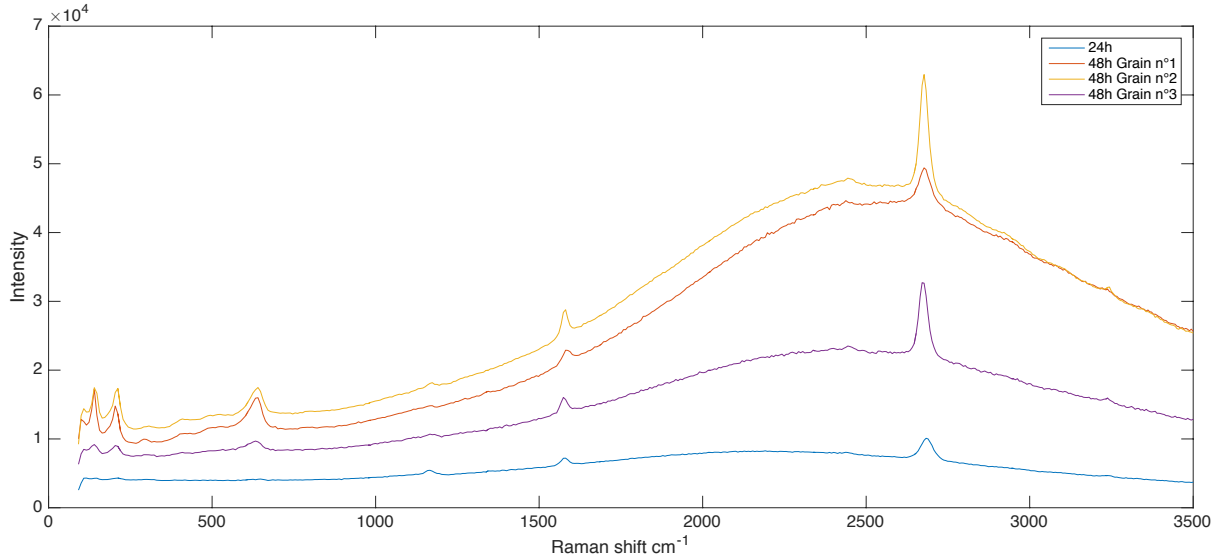


FIGURE 8.21 – Raman spectrum 24h and 48h

To analyze those spectrum, here below the table with their peaks, ratio and FWHM(2D).

Peaks	D [cm^{-1}]	G [cm^{-1}]	2D [cm^{-1}]	I_{2D}/I_G	FWHM(2D) [cm^{-1}]
24h	-	1581	2683	3.75	43
48h Grain n°1	-	1585	2679	2.5	35
48h Grain n°2	-	1577	2677	4	29
48h Grain n°3	-	1574	2674	5.5	30

TABLE 8.8 – Peaks, ratio peaks and FWHM(2D) for the wet oxidation

After 24 hours of oxidation, no peaks of oxidation are visible. The graphene flake is probably single layered because its FWHM(2D) is equal to 43 cm^{-1} . Its high ratio I_{2D}/I_G and the absence of the D peak mean that the oxidation does not affect its quality.

The flakes from the 48h wet oxidation are single layers of graphene with $25\text{ cm}^{-1} < \text{FWHM}(2D) < 35\text{ cm}^{-1}$. The quality of these flakes is unimpaired during the oxidation as, like after 24h wet oxidation, no D peak is visible and the I_{2D}/I_G ratio is still high. After 48 hours of oxidation, peaks of oxidation are visible. Furthermore, they all belong to the same type of oxidized copper, Cu_2O (109, 150, 217 and 644 cm^{-1}).

A peak is seen at 1166 cm^{-1} for each of those Raman spectrum. This peak could probably come from the hydrogenation of the graphene flake.

Finally, this oxidation is quicker than the dry one for the same temperature.

8.2 hBN preparation

The hBN is exfoliated with PDMS as scotch tape. After exfoliation, the hBN is needed either on SiO_2/Si for the acceptor substrate or on polymer(s)/support for the transfer mask (as mentioned in section 3.2.2).

8.2.1 Exfoliation of hBN with PDMS

The crystal of hBN is exfoliated by mechanical peeling with PDMS. The first step of the exfoliation process is the deposition of one crystal of hBN on a layer of PDMS. Since there are more than one crystal in the container full of hBN, a gently tap is enough to isolate one crystal close to the edge of the container and with some more gently taps to make it fall on the PDMS layer. Then, using an optical microscope (see Appendix C for microscopic view of the process) and a needle, the crystal is oriented so that its broadest side is in a parallel plane to the surface of the PDMS. After that, the first peeling is done by encapsulating the crystal with another PDMS layer. No pressure is needed and the disengagement rate must be slow. This operation is repeated many times to remove the stack of small layers that are not in a plane parallel to the PDMS surface. When a stack of large layers of hBN appears, the exfoliation process will really begin. A new PDMS layer is used. It will peel off the stack of the large layers thanks to a mechanical pressure and a quick peeling off movement. Then some layers of the stack will be peeled off by another PDMS layer and so on until a large flake not too thick (as mentioned in section 6.3.1) is isolated. To determine when to stop the exfoliation, the chosen flake needs a color close to that of the substrate (here the PDMS) as seen in Figure 8.22c and the edges of the flake have to be angular (Figure 8.22b) and not rounded (Figure 8.22a) which means that there is not too much flakes. This process takes place at room temperature.

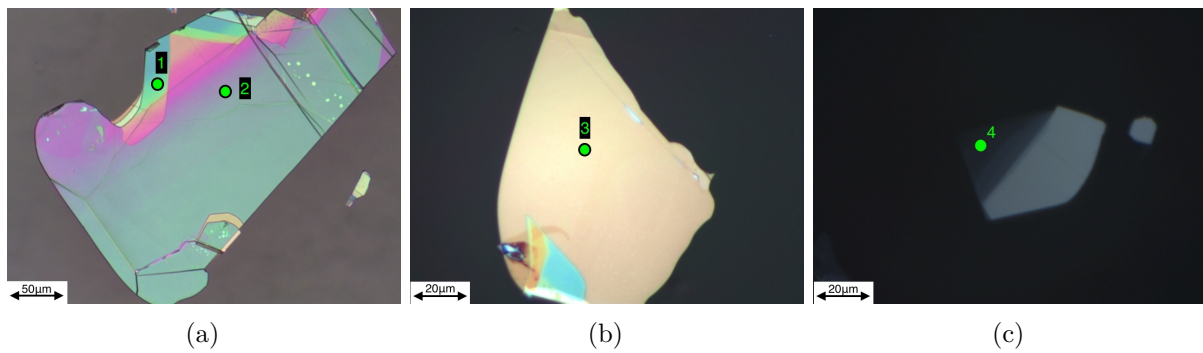


FIGURE 8.22 – Microscopic view of hBN flakes with different layer numbers on PDMS (the number of layers decreases from (a) to (c))

An analysis of the number of layers of those different hBN flakes is done by Raman spectroscopy. The results of the Raman spectrum (Figure 8.23) are given in the Table 8.9.

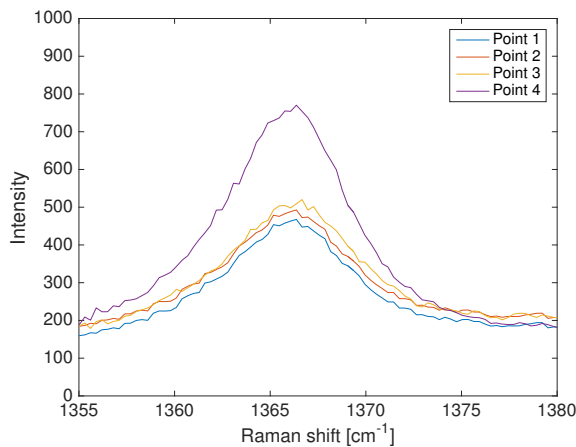


FIGURE 8.23 – Raman spectrum of hBN flakes with different layer numbers on PDMS

Point	Peak [cm^{-1}]	FWHM [cm^{-1}]
1	1366	6
2	1366	6
3	1366	6
4	1365	7

TABLE 8.9 – Peak and FWHM for hBN

The different hBN analysis are very similar. All the peaks are located at a shift of 1366 cm^{-1} and they have a FWHM of 6 or 7 cm^{-1} . These results are in agreement with what is expected from a bulk of hBN (namely 1366 cm^{-1} and a FWHM lower than 10 cm^{-1}). But this peak is supposed to shift to the left if the number of hBN layers decreases and reach the value of 1355 for a single layer of hBN. The peak is at the same shift (1366 cm^{-1}) for a thick hBN flake (Figure 8.22a) as for a thin one (Figure 8.22c). The only way to approximate this thickness is to use visual detection and choose a flake with the lowest possible contrast (like the one on Figure 8.22c).

8.2.2 Acceptor substrate: Exfoliated hBN on SiO_2

The transfer of the hBN flake from the PDMS to the SiO_2 takes place at ambient temperature. The result after contact depends on the mechanical pressure applied and on the delamination rate. If a pressure is applied, the hBN will not be picked up by the SiO_2 . Only with a slow peel-back and no pressure, the hBN will stay on SiO_2 (Figure 8.24a) as explained in section 3.2.2. The Figure 8.24b shows the first three peaks related to the Si and the last one to the hBN flake.

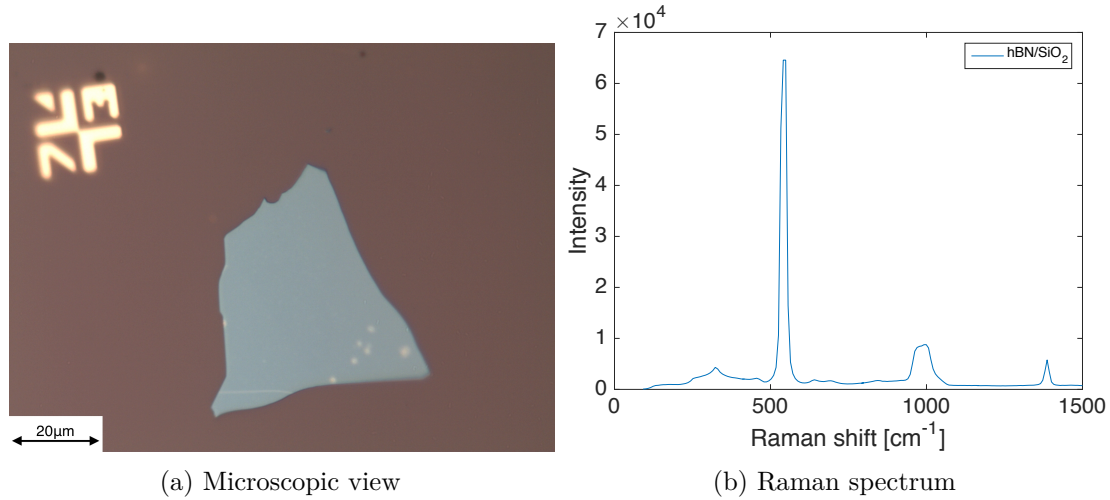


FIGURE 8.24 – Exfoliated flake of hBN on SiO_2

8.2.3 Transfer mask: Exfoliated hBN on PDMS

First, a piece of PDMS is placed on a glass slide while the hBN is exfoliated with other pieces of PDMS. Then the target hBN is encapsulated between its PDMS support and the PDMS on glass. To guarantee the picking up of the flake by the the PDMS on the glass, as mentioned in section 3.2.2, the PDMS support is slowly removed to leave the exfoliated hBN on the receiver, the PDMS/glass stack, that will be used as a transfer mask.

8.2.4 Transfer mask: Exfoliated hBN on PMMA/PDMS

The transfer mask used for the dry transfer is hBN/PMMA/PDMS/glass slide. Different orders of operations are studied.

If the PDMS is previously coated with PMMA before being pasted on the glass slide, induced stresses will tear the PMMA layer apart (Figure 8.25a) due to its rigid state at ambient temperature (as mentioned in section 6.3.2). But, if the PDMS is previously pasted on the glass slide before being coated, the PMMA layer will not tear apart. Sometimes PMMA is not distributed evenly (Figure 8.25b) but it is OK to work with.

So, the chosen solution is to spin-coat PMMA (4% solution) at 2000 rpm to ensure the best coating of the PDMS by PMMA.

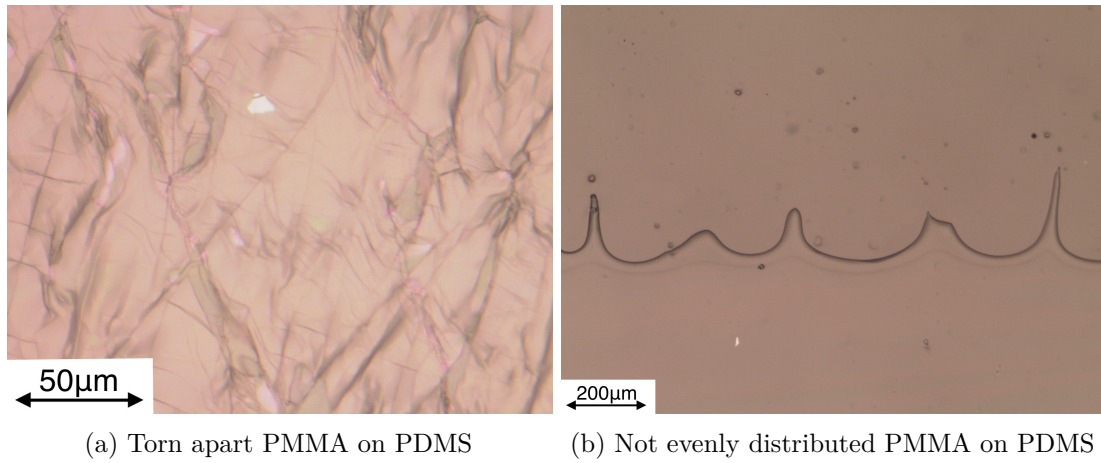


FIGURE 8.25 – Microscopic view of PMMA/PDMS/glass slide before contact with hBN/PDMS

The transfer of the exfoliated flake from the PDMS to the PMMA at ambient temperature involves also tearing of the PMMA (Figure 8.26a) again due to its rigid state at ambient temperature. The transparency is not so well preserved, and this adds difficulties during the transfer. To avoid tearing (Figure 8.26b), the transfer of the exfoliated hBN is heated up to 150 °C during 15 minutes at contact then immediately separated without cooling. The transparency is preserved.

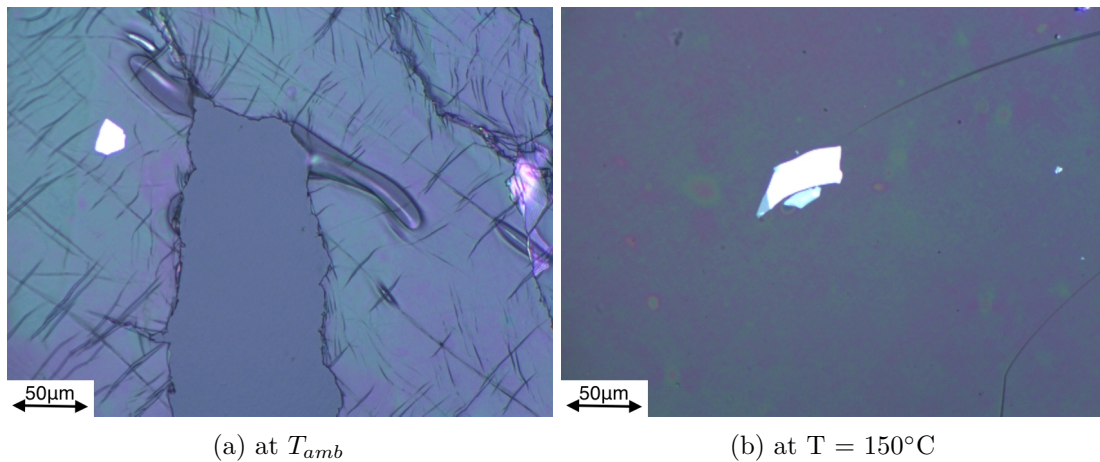


FIGURE 8.26 – Microscopic view of hBN/PMMA/PDMS after contact with PDMS

8.3 Wet transfer of graphene

A general presentation of wet transfer (with PMMA or PDMS as supporting layer) of graphene is presented at figure 8.27. Those wet transfers are mentioned in section 3.1.

First, a polymer (PMMA or PDMS) is deposited on the graphene/copper stack. Polymer/graphene/copper is then immersed in $FeCl_3$ that will etch the copper layer. When there is no more copper on the stack, polymer/graphene is placed on SiO_2/Si where hBN was previously placed or not. If the polymer used is PMMA, acetone will be needed to remove the polymer. If the polymer used is PDMS, a slow peel-back of the PDMS is sufficient to transfer the graphene from the PDMS to the acceptor substrate.

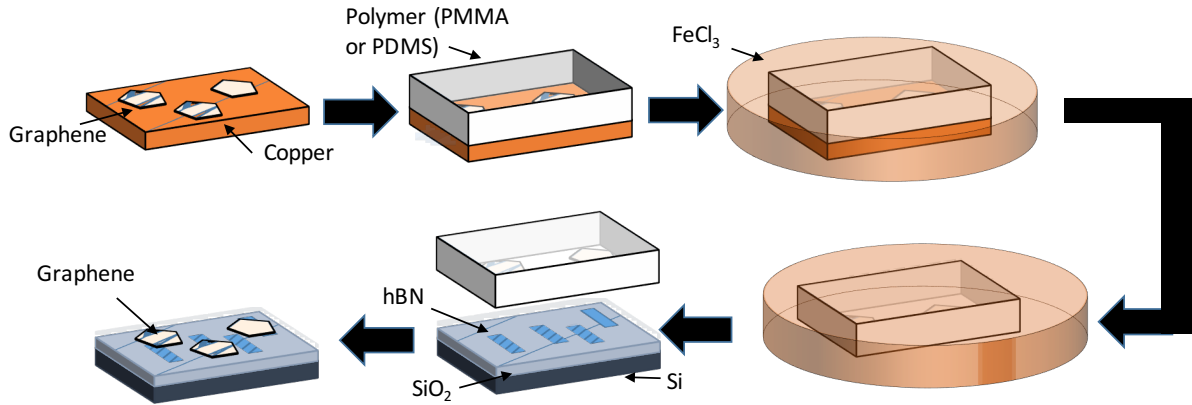


FIGURE 8.27 – Wet transfer of graphene on hBN with a supporting polymer

To compare the quality/mobility of the transferred graphene on SiO_2 or on hBN, Raman spectrum can be used. As mentioned in section 7.2.1, the graphene quality is related to the absence of the peak D and the ratios I_D/I_G and I_{2D}/I_G .

As explained in section 5.3, from Banszerus's research, the mobility of SLG on different substrates can be compared regarding the position and the FWHM of the peaks G and 2D. The larger the FWHM(G) and FWHM(2D), the higher the surface roughness, the higher the local strain fluctuation, the higher the disorder for high-quality graphene, the lower the charge carrier mobility. The Pos(G) and Pos(2D) can be shifted to the left or to the right due to the surface roughness of the substrate.

From Zhao's results, the higher the surface roughness, the bigger the shift to the left. On the other hand, Leon's results suggested that the downshift is related to the low doping of the graphene.

8.3.1 With PMMA

Hereafter, the results (microscopic view, Raman spectrum and analysis table) for a wet transfer of graphene on SiO_2 or on hBN/ SiO_2 with PMMA as support polymer.

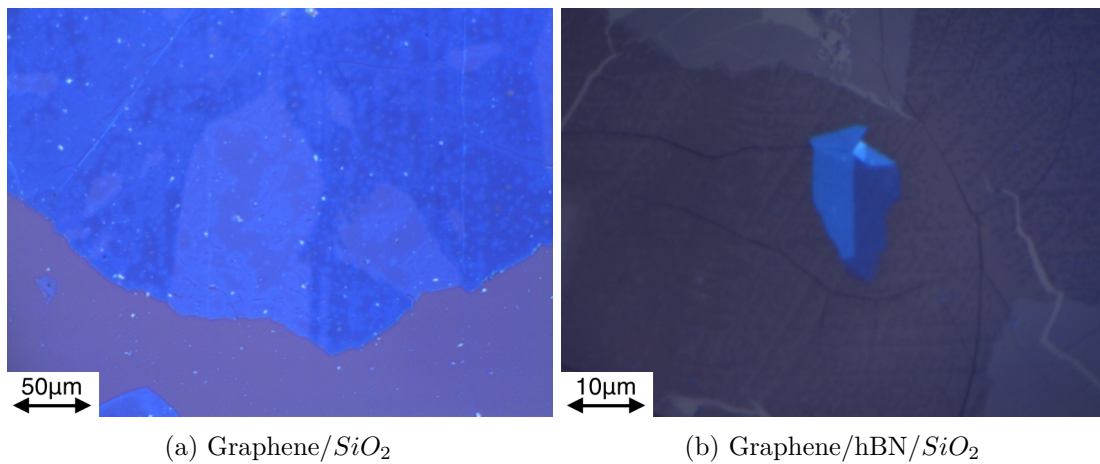


FIGURE 8.28 – Microscopic view of wet-transferred CVD graphene flake on different acceptor substrate with PMMA as support polymer

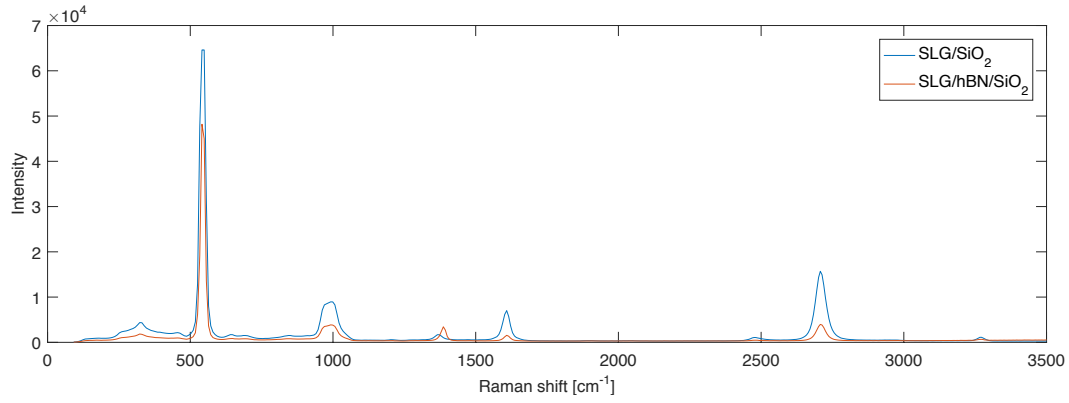


FIGURE 8.29 – Raman spectrum of Graphene/ SiO_2 and Graphene/hBN/ SiO_2 from wet transfer with PMMA

The results of the Raman spectrum (Figure 8.29) are given in the Table 8.10.

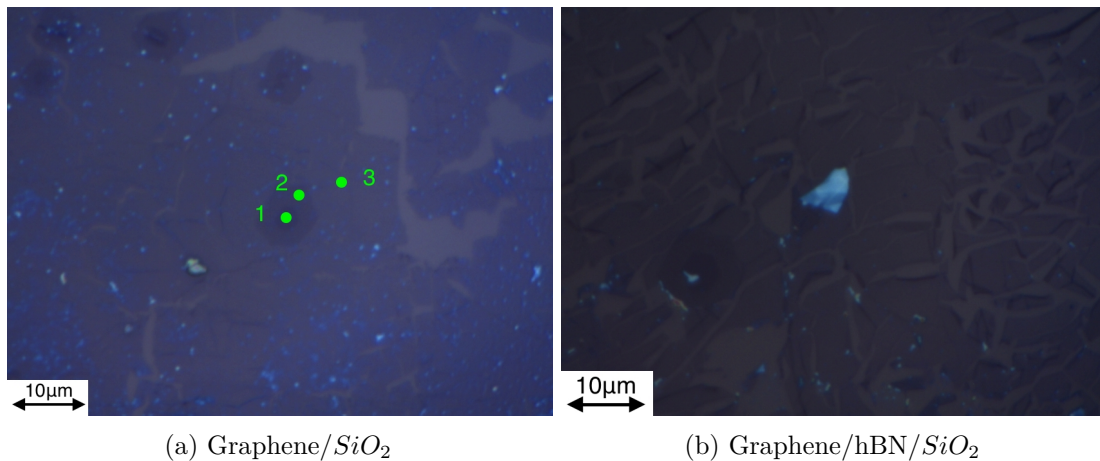
Peaks	Pos(D) [cm^{-1}]	Pos(G) [cm^{-1}]	FWHM(G) [cm^{-1}]	Pos(2D) [cm^{-1}]	FWHM(2D) [cm^{-1}]	I_D/I_G	I_{2D}/I_G
SLG/ SiO_2	1368	1608	28	2707	43	0.18	2.14
SLG/hBN/ SiO_2	1386	1608	24	2710	37	-	2.2

TABLE 8.10 – Peaks, Ratio peaks and FWMH for the wet transfer with PMMA

In Table 8.10, the width of both peaks G and 2D are sharper for hBN than for SiO_2 . The Pos(2D) is more to the left for SiO_2 . This means that the mobility of the SLG/hBN/ SiO_2 is higher than the one of SLG/ SiO_2 . The presence of the D peak for the SLG/ SiO_2 has a meaning of defect. But for the SLG/hBN/ SiO_2 , there is an overlapping of the hBN peak and the D-peak that impede their differentiation and therefore their respective intensity and their interpretation.

8.3.2 With PDMS

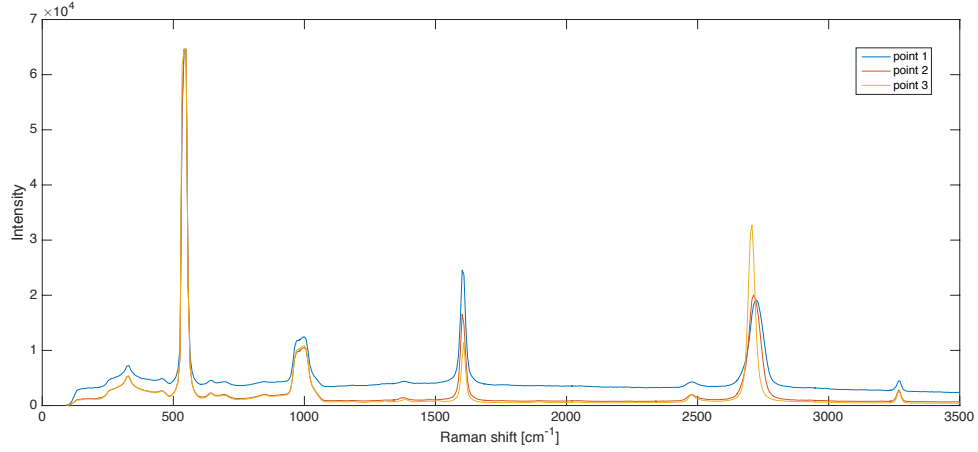
Hereafter, the results (microscopic view, Raman spectrum and analysis table) for a wet transfer of graphene on SiO_2 or on hBN/ SiO_2 with PDMS as support polymer.



(a) Graphene/ SiO_2

(b) Graphene/hBN/ SiO_2

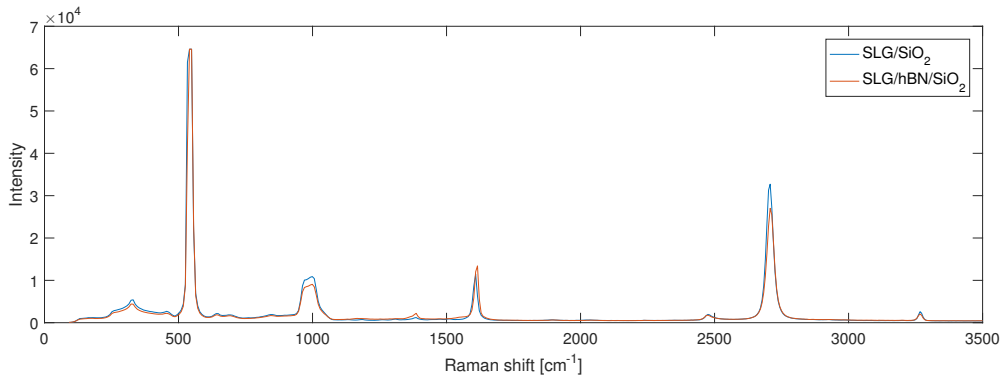
FIGURE 8.30 – Microscopic view of wet-transferred CVD graphene flake on different acceptor substrate with PDMS as support polymer

FIGURE 8.31 – Raman spectrum of Graphene/ SiO_2 from wet transfer with PDMS

Peaks	D [cm^{-1}]	G [cm^{-1}]	2D [cm^{-1}]	I_{2D}/I_G	FWHM(2D)
point 1	1388	1606	2725	0.75	70
point 2	1372	1602	2715	1.17	45
point 3	1386	1608	2705	3	30

TABLE 8.11 – Peaks, ratio peaks and FWHM(2D) for the wet transfer with PDMS for different number of layers

Three shades of blue can be observed in Figure 8.30a. By visual detection, it can be determined that the darker blue shade is the nuclei of the flake (point 1) and the lighter blue is a monolayer of graphene (point 3). By an analysis of the Raman spectrum, with the ratio of the peaks I_{2D}/I_G , the position and the FWHM of the 2D peak, the number of layers can be determined. What is expected: a decrease of the ratio, a widening and an up-shifting of the 2D peak with an increase of the number of layers (as mentioned in section 7.2.1). The results of the Raman spectrum (Figure 8.31), given in the Table 8.11, are in agreement with those expectations.

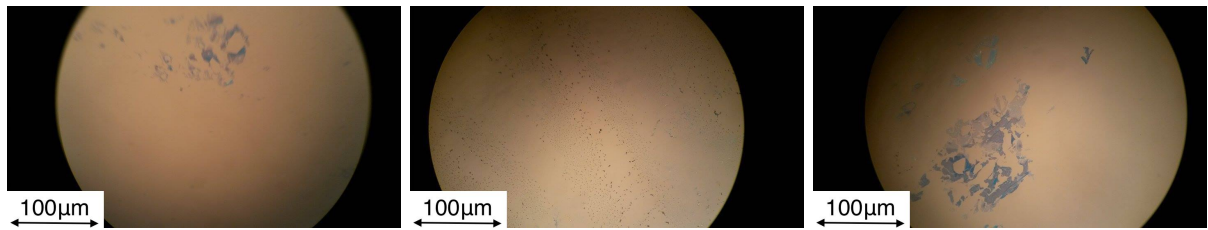
FIGURE 8.32 – Raman spectrum of Graphene/ SiO_2 and Graphene/hBN/ SiO_2 from wet transfer with PDMS

The results of the Raman spectrum (Figure 8.32) are given in the Table 8.12.

Peaks	Pos(D) [cm^{-1}]	Pos(G) [cm^{-1}]	FWHM(G) [cm^{-1}]	Pos(2D) [cm^{-1}]	FWHM(2D) [cm^{-1}]	I_D/I_G	I_{2D}/I_G
SLG/ SiO_2	1386	1610	17	2705	30	0.05	3.2
SLG/hBN/ SiO_2	1387	1615	17	2708	31	-	2.2

TABLE 8.12 – Peaks, Ratio peaks and FWMH for the wet transfer with PDMS for different substrates

In term of the position of the G-peak (pos(G)), it is more to the left for SLG/ SiO_2 than for SLG/hBN/ SiO_2 due to the surface roughness of the substrate. It is the same for pos(D). The electronic mobility of the SLG/hBN/ SiO_2 should therefore be the greatest.



(a) Graphene on SiO_2 from Cu/Gr oxidized (200 °C, 1h30) (b) Graphene on SiO_2 from Cu/Gr oxidized (200 °C, 6h) (c) Graphene on SiO_2 from Cu/Gr oxidized (200 °C, 48h)

FIGURE 8.33 – Microscopic view of failed wet-transferred CVD graphene flake on SiO_2 with PDMS as support polymer

In Figure 8.33, some failed tests of wet transfer of graphene with PDMS on SiO_2 can be seen. The rinsing part was as crucial as the peeling rate. Indeed, if the PDMS stack is immersed in water and not just rinsed, it separates itself from its support layer and folds in the water. This also provokes the folding of the graphene and its separation from the PDMS in the water, resulting in a broken sample.

8.3.3 PMMA vs PDMS

A comparison can be made between the two wet transfers with the results given in Table 8.10 and Table 8.12.

For the ratio I_D/I_G , it is higher for the wet transfer with PMMA than with PDMS, 0.18 and 0.05 respectively.

For the ratio I_{2D}/I_G , it is lower for the wet transfer with PMMA than with PDMS, 2.14 and 3.2 respectively. This could mean that there are less defects in the wet-transferred graphene that was in contact with PDMS than in the one in contact with PMMA and acetone.

The FWHM are sharper for the wet transfer with PDMS than with PMMA thanks to less residues. Also, the positions are more downshifted (to the left) for PDMS.

In conclusion, the wet transfer with PDMS seems to give more convincing results.

8.4 Dry transfer of graphene on polymer

In this transfer technique, hBN flakes are first placed on SiO_2 as the acceptor substrate. On the other hand, graphene flakes are on the polymer layer as the transfer mask (see section 3.2.6). The two stacks can be seen in Figure 8.34.

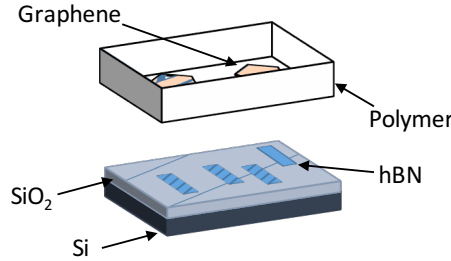


FIGURE 8.34 – Stacks before dry transfer of CVD-graphene/polymer on hBN/ SiO_2 /Si

To obtain the stack graphene/polymer, 3 different methods were tested:

- Delamination of CVD graphene, first wet-transferred on a SiO_2 /Si slice, with PDMS
- Delamination of CVD graphene from its growth substrate (Cu) with PDMS
- Delamination of CVD graphene from its growth substrate (Cu) with PMMA/PDMS stack

These 3 different transfer techniques of graphene/copper to polymer are commented in the following subsections.

8.4.1 Delamination of graphene from SiO_2 with PDMS

To ensure a good delamination of the graphene with the PDMS, the adhesion energy between PDMS and graphene needs to be greater than the one between graphene and SiO_2 .

As mentioned in section 3.2.2, the adhesion energy of the PDMS is related to its delamination rate and its temperature. To measure this adhesion energy, graphene was placed on a substrate for which the adhesion energy is known, then a trial of delamination was performed. If the delamination happens, it means that the energy between PDMS and graphene is larger than between the substrate and graphene.

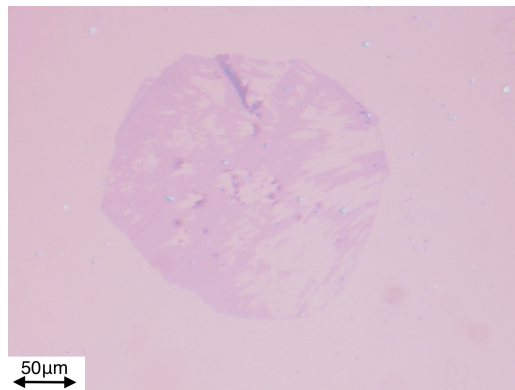


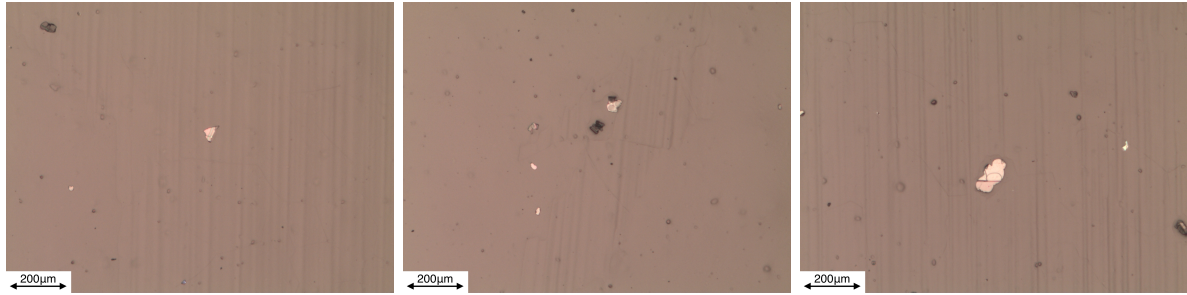
FIGURE 8.35 – Remains of wet-transferred graphene on SiO_2 after peeling by PDMS

The Figure 8.35 shows a partial delamination, at ambient temperature and with a quick rate, of the graphene flake that was previously wet-transferred on the SiO_2 .

8.4.2 Delamination of graphene from copper with PDMS

The problematic is the same, as in the previous section, for picking up the graphene from the copper and so the same methodology was applied.

At ambient temperature, nothing happened. At higher temperature (e.g., 100°C) after a long period (2-4 hours), an fingerprint is left on the PDMS after contact (Figure 8.36). The grain of copper had left a mark caused by the softening of the PDMS during heating. It helps to locate the contact with the graphene flakes.



(a) After contact at 100°C during 1h30 (b) After contact at 100°C during 3h30 (c) After contact at 100°C during 4h30

FIGURE 8.36 – Microscopic view (x20-raman) of PDMS after contact with Gr/Cu

8.4.3 Delamination of graphene from copper with PMMA

The contact of the PMMA on the graphene can be achieved by different ways:

- Deposition of a drop of PMMA on the graphene
- Spin-coating of PMMA directly on the graphene
- Spin-coating of PMMA on PDMS then putting PMMA/PDMS and graphene into contact

As explained in section 3.2.2, the temperature (heating/cooling), the delamination speed and, the mechanical pressure could have an impact of the transfer. Tests were made for different temperatures (ambient, 100°C, 125°C and 150°C), with or without mechanical pressure at contact, with or without cooling before disengagement and, with a quick or slow delamination rate.

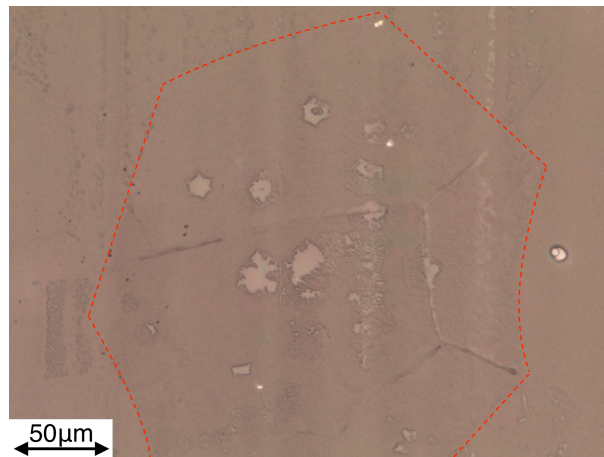


FIGURE 8.37 – After contact of PMMA/PDMS and Gr/Cu_{ox}

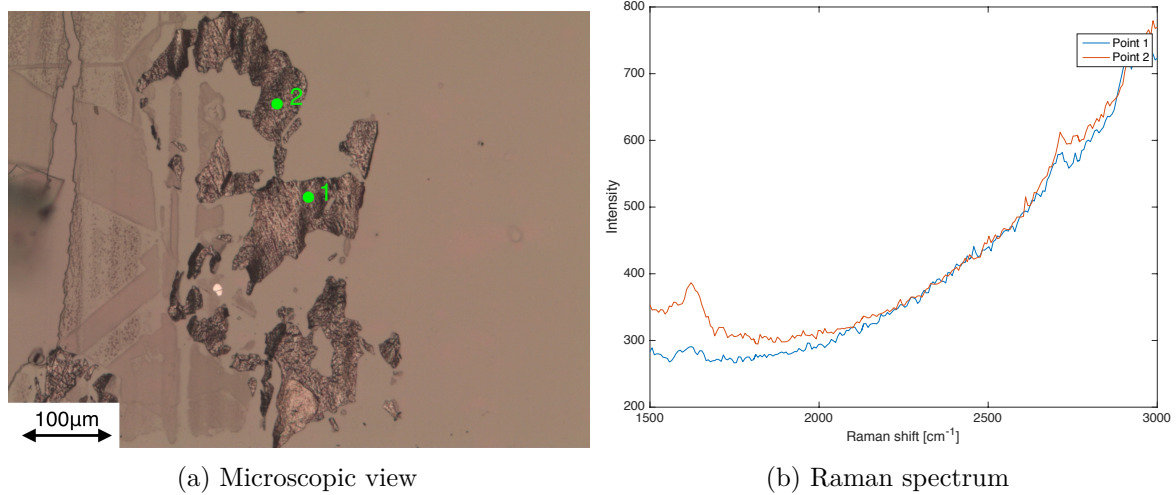


FIGURE 8.38 – Graphene transferred on PMMA

An fingerprint (Figure 8.37) and a delamination (Figure 8.38a) took place at 125°C and with a mechanical pressure during contact, with cooling before a slow delamination rate for a PMMA/PDMS that was deposited on the thermal annealed graphene during 39 hours at 200°C.

Regarding the peaks observed in the Raman spectrum (Figure 8.38b), it could possibly be graphene.

8.5 Dry transfer of graphene with hBN on polymer

In this type of dry transfer technique (as explained in section 3.2.9), CVD graphene is directly picked off from its growth substrate (copper) as seen in Figure 8.39. The substrate was first oxidized to reduce adhesion energy between graphene and copper. The polymer layer may either be PDMS or a PMMA/PDMS stack.

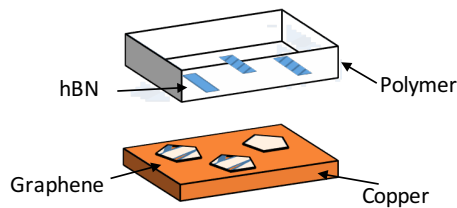


FIGURE 8.39 – Stacks before dry transfer of CVD-graphene/copper on hBN/polymer

8.5.1 Transfer process

A schematic representation of the transfer process can be seen in Figure 8.40.

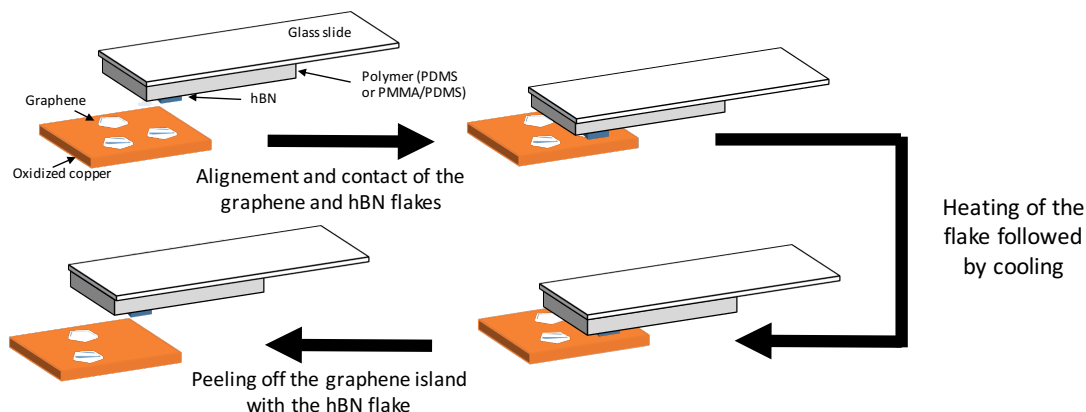


FIGURE 8.40 – General approach of a dry transfer

At the end of this process, graphene should be picked up by the flake, but it did not happen during the experiments we performed. hBN was sometimes released from the polymer and sometimes no flakes transfer happened at all.

For the dry transfer with PDMS, transfer without heating were tried in order to pick up the graphene flake.

For the dry transfer with PMMA, transfer with heating during contact at 120°C was tried in order to pick up the flake. Once this temperature was reached, it took 15 to 20 minutes for the PMMA to become soft. After 30 min, the contact surface was cooled in ambient air during 6 hours. Then the stack was separated with a slow displacement rate (100 $\mu\text{m/s}$). If the transfer had taken place, that process would have been followed by another transfer of the two flakes on hBN/ SiO_2 but this time with a temperature of 140 °C in order to release the flakes from the polymer stack.

Here after in Figure 8.41, the microscopic view before (Figure 8.41a and Figure 8.41b) and after contact (Figure 8.41c) of the transfer mask and the acceptor substrate.

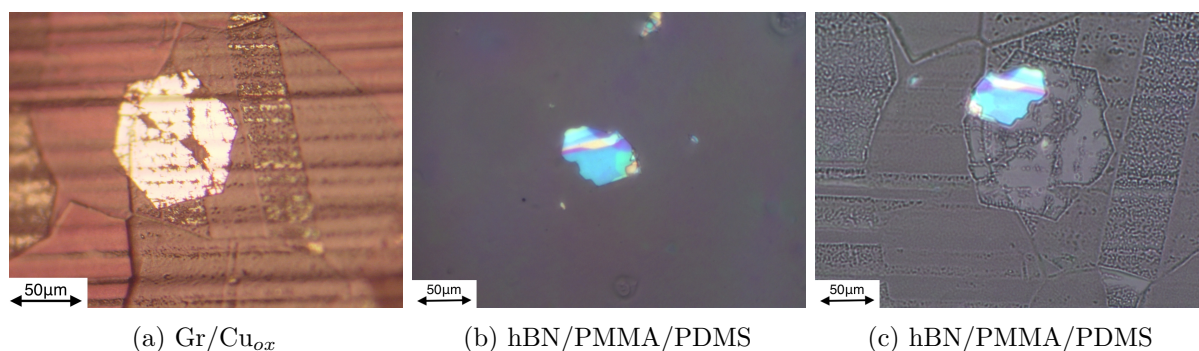


FIGURE 8.41 – Microscopic views before and after contact of hBN/PMMA/PDMS and Gr/Cu (oxidized during 39h at 200°C)

8.5.2 Step by step

Choice of the flakes

First, the graphene and hBN flakes are chosen. Graphene on a Cu_2O oxidized copper (Figure 8.42) and hBN thicker than 5 nm but not too thick (Figure 8.43). The flakes are chosen to have a size as similar as possible but with the hBN flake a bit bigger than the graphene flake.

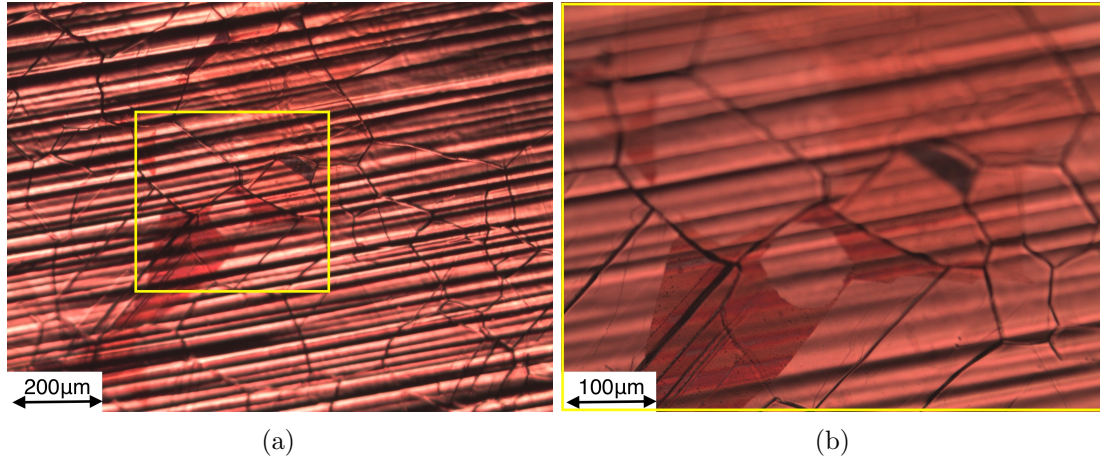


FIGURE 8.42 – Graphene islands on oxidized copper substrate

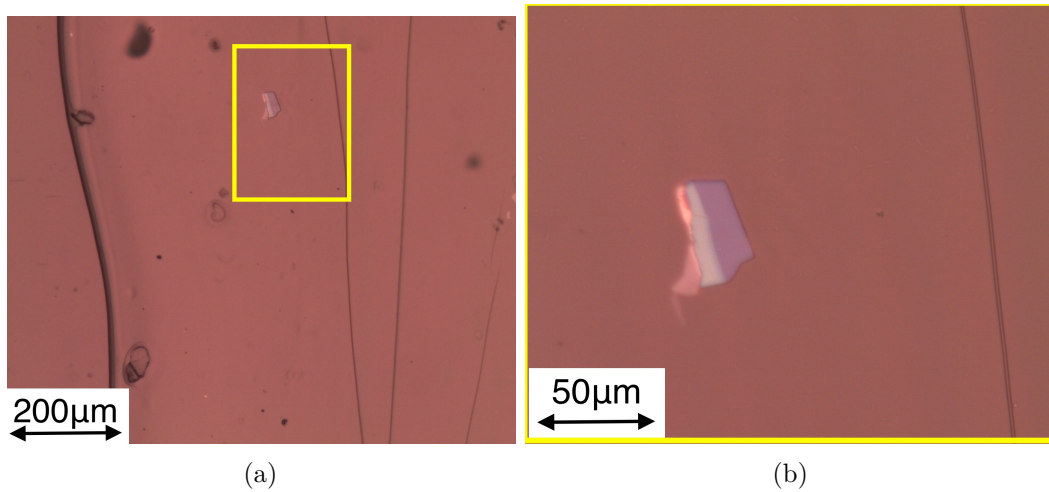
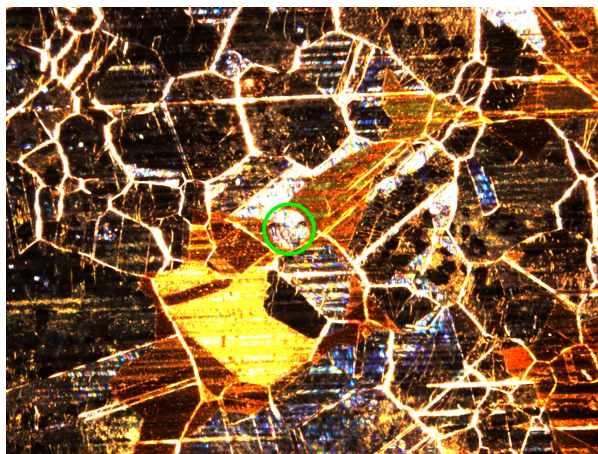


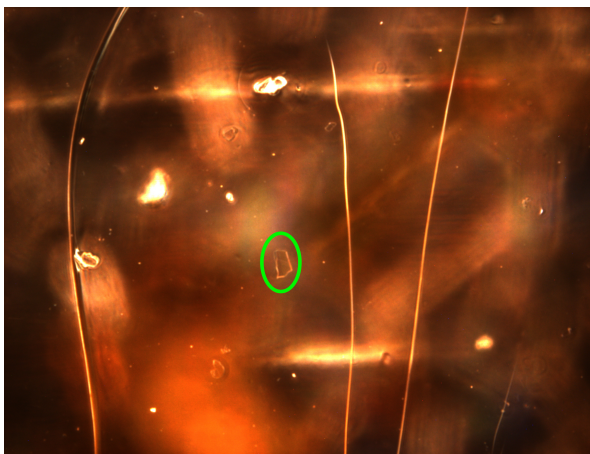
FIGURE 8.43 – hBN flake on polymer(s)

Alignment and contact between the flakes

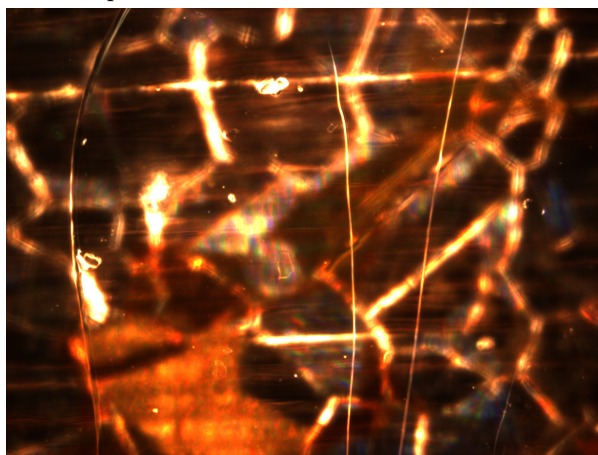
The two flakes which will intervene in the transfer are previously chosen with a classic microscope. Graphene on copper foil and hBN/polymer/glass slide are placed on the micromanipulator. The flakes are identified with the long focal distance microscope (Figure 8.44a and 8.44b). They are then aligned with the help of the micromanipulator (Figure 8.44c). When they are perfectly aligned, hBN flake is gently moved down to graphene and the best contact between the two layers is realized (Figure 8.44d). When contact is ensured, temperature of the package is raised to 125°C to loosen the PMMA layer (Figure 8.44e). After cooling down, the two stacks are separated at a speed close to $100 \mu\text{m/s}$. It can be seen in Figure 8.44f that the PMMA layer takes shape of the copper, and some bounds of the copper grain left an fingerprint on PMMA.



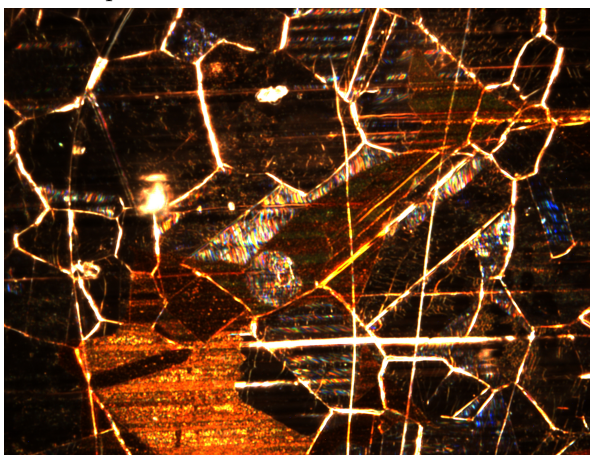
(a) Graphene flake is identified on long focal distance microscope



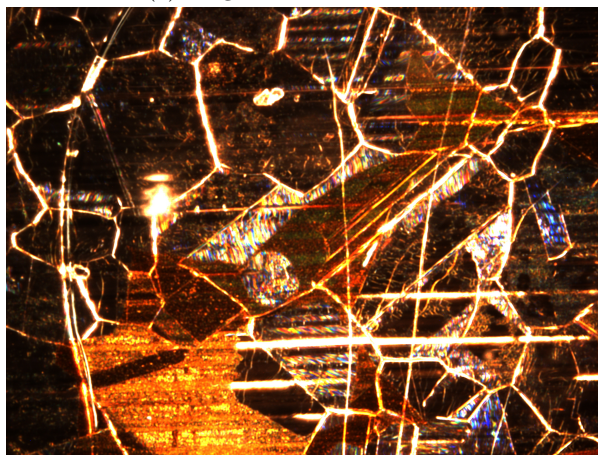
(b) hBN flake is identified on long focal distance microscope



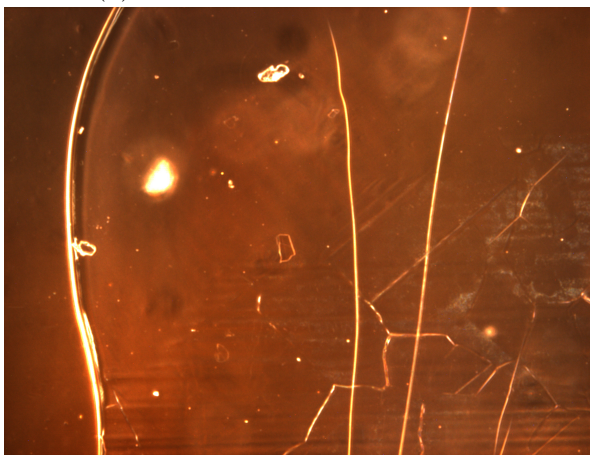
(c) Alignment of the flakes



(d) Contact between the two flakes



(e) Heating up to 125°C



(f) Separation of the stacks

FIGURE 8.44 – General process of a dry transfer

8.6 Discussions

To conclude this chapter, the main results are summarized and discussed here:

- The **minimization** of the adhesion between graphene and its substrate by oxidation.

When the wet oxidation process is performed at a temperature exceeding 150°C , different types of Cu oxides (Cu_2O , CuO , $\text{Cu}(\text{OH})_2$) are formed. These oxides give the Cu surface a brownish color which can be observed with bare eyes. In contrast, oxidizing the Cu substrate below 100°C exclusively result in Cu_2O , which gives the Cu surface a reddish tone.

As these different oxides/hydroxides have a different surface energy, they do not adhere to graphene with the same energy. As CuO_2 exhibits the lowest surface energy, optimizing its formation at the expense of other oxides/hydroxides is crucial to reduce the adhesion of graphene on the substrate. Given the rough surface morphology of the Cu substrate and the impermeability of graphene to $\text{H}_2\text{O}/\text{O}_2$ gases, the oxidation of Cu underneath the graphene domains is not uniform. Moreover, the Cu surface crystallographic orientation also impacts the adhesion of graphene on its substrate, and thus influences the propagation of the oxidation front. This observation is particularly critical given that prolonged exposure to $\text{O}_2/\text{H}_2\text{O}$ can adversely impact the graphene purity/integrity. So, to obtain a deeper oxidation, wet oxidation was performed with water. Those oxidations are quicker than dry oxidation.

As a consequence, a graphene domain grown on Cu(111) will be preferably selected for the delamination. This Cu surface will thus be oxidized under low temperature in order to only grow Cu_2O at the Cu/Graphene interface.

- The **maximization** of the adhesion between graphene and its transfer mask.

If the transfer mask is a polymer, the temperature and the delamination rate have a direct impact on its adhesion energy. If the transfer mask is a pre-deposited flake of hBN on a polymer, then an increase of temperature could increase the contact surface area enhancing the adhesion between the flakes. To guarantee the alignment of the flakes before contact, the transfer mask needs to be transparent. A fabrication process was proposed.

- The **visualization** of graphene on polymer.

If the temperature is increased up to the T_g of the polymer before delamination, then an fingerprint stays on the polymer which is helpful to precisely locate the position of the graphene on the polymer.

- The **dry transfer** techniques.

Two different methods seem to be feasible if the temperature, the transfer mask-to-graphene distance and the delamination rate are precisely controlled.

- The **mobility** on hBN substrate.

Wet-transferred graphene on hBN and on SiO_2 were compared. Transferring graphene on hBN gives better results in term of mobility according to the FWHM of 2D Raman peak.

In summary, the process parameters playing a critical role in successfully dry transferring graphene are:

- **For minimizing adhesion substrate/graphene**
 - Cu grain orientation
 - Presence and type of underlying Cu oxides
- **For maximizing adhesion hBN/graphene or polymer/graphene**
 - Choice of polymer
 - Delamination rate
 - Heating/cooling (rates and duration) during contact
 - Pressure during contact
 - Distance between graphene and hBN
 - Surface roughness

Conclusion

The aim of this work was to transfer in a dry manner chemically vapor deposited graphene on hBN in order to fully exploit its potential and benefit from its extraordinary physical properties.

Therefore, a careful study of the literature about graphene, hBN, transfer techniques, adhesion energy of graphene and the electronic mobility has been conducted.

A great deal of effort has been made in order to reduce the adhesion of graphene on its synthesis substrate. This has been done by mildly oxidizing the Cu surface while maintaining the high structural quality of graphene. Improvements have been achieved in wet and dry transfer techniques to tend to the cleanest transfer of graphene on hBN.

Raman spectroscopy and optical microscopy has been the major characterization tools employed for this master's thesis.

Main results

From the comparison of wet-transferred graphene on hBN and on SiO_2 , graphene on hBN gives better results in term of mobility according to the FWHM of 2D Raman peak. Using hBN as the insulator underlying substrate could allow graphene to reach its highest electronic mobility.

Oxidation is performed in order to reduce the adhesion energy between graphene and its growth substrate while keeping its high integrity/quality. From literature, cuprous oxide (Cu_2O) is the copper oxide with the lowest surface energy and then could adhere less to graphene. Various oxidation experiments have been carried out with varying parameters including the oxidizing agent (H_2O or O_2), the temperature and the process duration. A wet oxidation at a temperature of 60 °C yields the best results in terms of Cu oxidation and graphene structural quality. It has been shown in this work that an oxidation during 48 hours induces a complete oxidation of graphene-covered copper.

Several methods of dry transfer of graphene with a delamination by polymer were tested: a dry transfer of graphene with a polymer and a hBN-assisted dry transfer of graphene. Parameters were defined thanks to a delamination experiment of graphene that succeeded. PMMA and PDMS were used as receiver layer to peel off the graphene from its growth substrate.

PMMA adheres more than PDMS to graphene because of its the ability to soften and conform due of its glass transition temperature T_g ($T_{g(PMMA)} > T_{g(PDMS)}$). The rate and temperature delamination have an impact on the success of the process. If the temperature at contact is bigger than the glass transition temperature of the PMMA ($T_g = 100^\circ\text{C}$), the polymer will soften, fit the shape of the flake and so adhere more after the cooling of the transfer.

A delamination of graphene appeared for a flake on copper oxide of Cu_2O with PMMA as receiver layer, a mechanical pressure and a heating and cooling at contact, but the hard control of all these parameters makes this technique a hardly reproducible process.

Prospects

For a future work, the key of the success for a good hBN-assisted dry transfer would be a better control of the delamination rate. The selection of the graphene flake is also a critical parameter, the graphene flake has to be on a grain of copper with the good orientation (111) to not adhere to it too much. The size of the hBN flake could also impact the process. A flake of hBN a bit bigger than the flake of graphene is recommended.

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Appendix A

Young's modulus and Poisson's ratio of graphene/graphite

References	Materials	E [TPa]	ν	Method
Frank, 2007 [139]	Graphene	0.5		AFM
Lee, 2008 [140]	Graphene Graphite	1	0.165	AFM
Koenig, 2011 [74]	Graphene	1		Blister
Blakslee, 1970 [141]	Graphite		0.16	Static
Lee, 2012 [142]	SLG BLG	2.4 2		Raman Raman

TABLE A.1 – Common values of Young's modulus (E) and Poisson's ratio (ν) from literature

Appendix B

Adhesion Energy Models

Relation can be made between the contact radius a , the sample deformation δ and the adhesion force F_{adh} for a spherical tip on a flat surface according to the Hertz, Johnson-Kendall-Roberts (JKR) and Derjaguin-Muller-Toporov (DMT) models (Table B.1).

	Hertz	DMT	JKR
a	$\sqrt[3]{\frac{RF}{E_{tot}}}$	$\sqrt[3]{\frac{R}{E_{tot}}(F + 2\pi RW)}$	$\sqrt[3]{\frac{R}{E_{tot}} \left(F + 3\pi RW + \sqrt{6\pi RW F + (3\pi RW)^2} \right)}$
δ	$\frac{a^2}{R} = \left(\frac{F^2}{RE_{tot}^2} \right)^{1/3}$	$\frac{a^2}{R} = \frac{(F + 2\pi RW)^{2/3}}{\sqrt[3]{RE_{tot}^2}}$	$\frac{a^2}{R} = \frac{2}{3} \sqrt{\frac{6\pi W a}{E_{tot}}}$
F_{adh}	0	$2\pi RW$	$\frac{3\pi RW}{2}$

TABLE B.1 – Hertz, JKR and DMT models

with R the tip radius, W the adhesion work per unit area, F the force exerted by the tip on the surface and E_{tot} the reduced Young's modulus defined as

$$\frac{1}{E_{tot}} = \frac{3}{4} \left(\frac{1 - \nu_s^2}{E_s} + \frac{1 - \nu_t^2}{E_t} \right)$$

with ν_t , E_t , ν_s and E_s the Poisson's ratios and the Young's modulus of the tip and the sample.

The adhesion between the sample and the tip is neglected in Hertz model. JKR model can be applied for large tips and soft samples with a large adhesion. DMT model can be applied for small tips and stiff samples with a small adhesion [68].

Maugis proposed, in 1992, a better approximation with its Maugis-Dugdale theory:

$$W_{adh} = \frac{F_{adh}}{\lambda \pi R_{tip}}$$

with λ an effective coefficient (1.66 for SiO_2 , 1.77 for Cu) [70].

One of the last model proposed is the modified Rumpf model:

$$W_{adh} = \frac{F_{adh}}{\lambda\pi R_{tip}} \frac{(1 + \frac{R_{tip}}{1.48R_{atomic}})^{-1} + (1 + \frac{1.48R_{atomic}}{z_0})^{-2}}{(1 + \frac{R_{tip}}{1.48R_q})^{-1} + (1 + \frac{1.48R_q}{z_0})^{-2}}$$

with R_{atomic} the roughness of atomically flat surface (0.03 nm), z_0 the equilibrium separation of the surface (0.3 nm for Gr/ SiO_2 and 0.36 nm for Gr/Cu) and R_q the tip RMS roughness [70].

Appendix C

Exfoliation of hBN

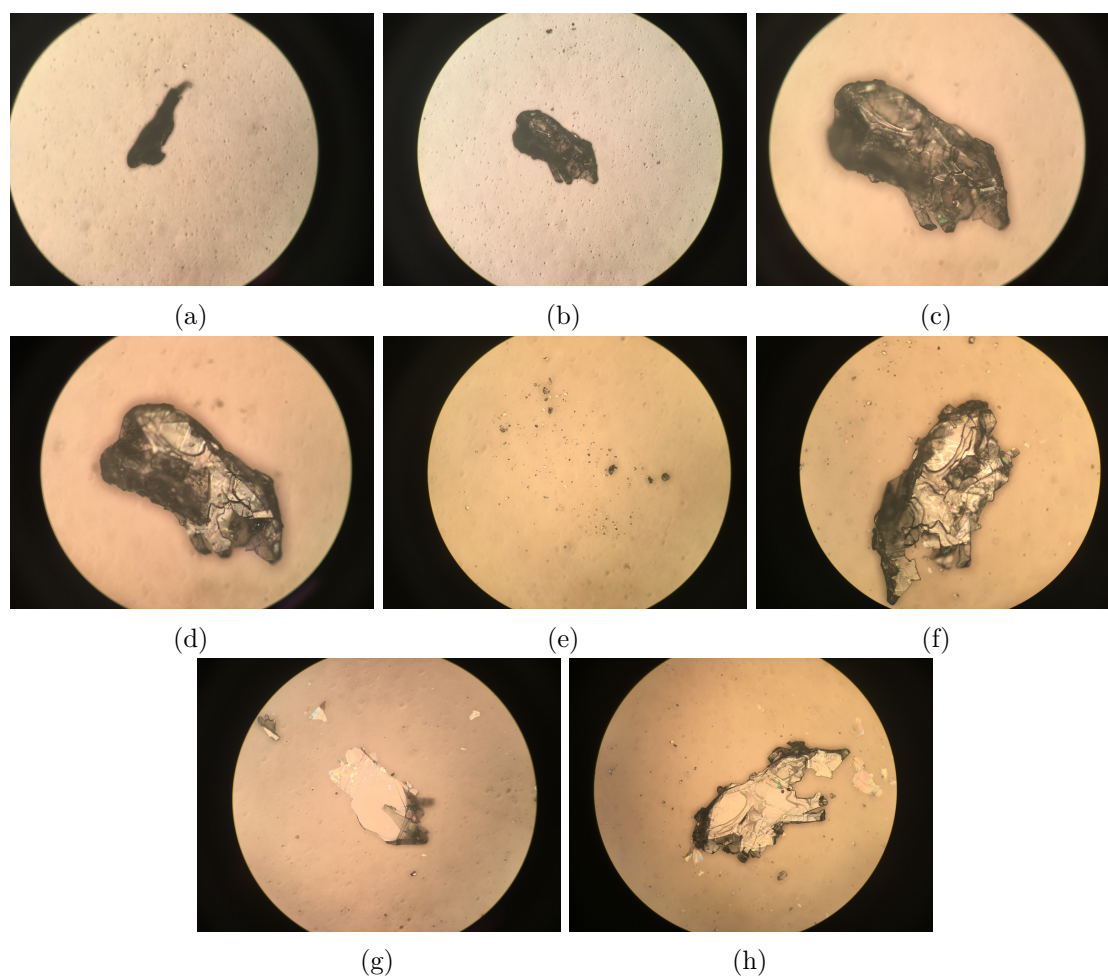


FIGURE C.1 – Microscopic view of the exfoliation of a hBN powder from (a) to (h)

As seen in Figure C.1a, the powder does not adhere immediately to the PDMS with its larger side. With a needle, a gentle push is enough to place the powder on its larger side (Figure C.1b). An exfoliation of the powder (Figure C.1c) with a new PDMS leaves the powder thinner (Figure C.1d) with less stacks of flakes. The flakes that were delaminated are not always big flakes (Figure C.1e). This last step is repeated in Figure C.1f until the stacks that are exfoliated are no more stacks of tiny flakes but stacks of bigger flakes as in Figure C.1g leaving the starting powder again a little thinner (Figure C.1h).

